# WASTE MINIMIZATION AND PROCESS INTEGRATION APPLIED TO THE RETROFIT DESIGN OF CHEMICAL PROCESSES

By

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Mauricio Dantus

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# NOMENCLATURE

## Roman letters

| | |
|---|---|
| $a$ | Temperature exponent |
| $A$ | Pre-exponential factor |
| $A_v$ | Area of vessel |
| $Ac$ | Additional costs |
| $Ap$ | Annual operating costs |
| $Au$ | Annual cost of utilities |
| $b$ | Exponent |
| $B,\ \overline{B}$ | Index set of Boolean variables |
| $c$ | Objective function |
| $C$ | Concentration |
| $CF$ | Fixed capital cost |
| $C_L$ | Shift earning per hour |
| Cs | Utility cost |
| $D$ | Diameter |
| $D_f$ | Depreciation factor |
| $E$ | Henry's law parameter |
| $E_{\mathrm{a}}$ | Activation energy |
| $Ep$ | Economic performance |
| $f$ | Flowrate |
| $F$ | Future value |
| $F_c$ | Design factor |
| $f_D$ | Discount factor |
| $F_d$ | Design type factor |

| | |
|---|---|
| $F_m$ | Design material factor |
| $F_p$ | Design pressure factor |
| $g$ | Matrix of inequality constraints |
| $H$ | Henry's law constant |
| $H_1, H_2$ | Henry's law parameter |
| $h$ | Matrix of equality constraints |
| $i$ | Interest rate |
| $I$ | Cold streams |
| $In$ | Income |
| $J$ | Hot streams |
| $K$ | Separator sizing factor |
| $L$ | Length |
| $M$ | Subset of 0-1 variables that are treated as continuous |
| $m$ | Number of integer variables |
| $Mc$ | Manufacturing costs |
| $N$ | Node under examination |
| $n$ | Number of continuous variables |
| $No$ | Number of operators |
| $ny$ | Number of years |
| $O$ | Operating costs |
| $P$ | List of open nodes |
| $Q$ | Heat load |
| $Q_A$ | Volumetric flowrate |
| $Q_v$ | Capacity |
| $q$ | Index of next variable to be branched |
| $R$ | Gas constant |
| $Rw$ | Raw material costs |
| $r$ | Rate of reaction |
| $s$ | Service life |
| $S_0$ | Set of binary variables to be fixed at 0 |

| | |
|---|---|
| $S_1$ | Set of binary variables to be fixed at 1 |
| $T$ | Temperature |
| $Tx$ | Tax rate |
| $U$ | Overall heat transfer coefficient |
| $V_t$ | Terminal gas velocity |
| $W$ | Waste costs |
| $x$ | Continuous variables |
| $y$ | Integer variables |
| $Y_i$ | Existence of unit $i$ |
| Z | Mixer and splitter blocks |
| $z$ | Lower bound |
| $Z^u$ | Upper bound |

Greek letters

| | |
|---|---|
| $\Delta c$ | Differential profit |
| $\Delta T_1$ | Temperature difference at hot end of heat exchanger |
| $\Delta T_2$ | Temperature difference at cold end of heat exchanger |
| $\Delta T_{min}$ | Minimum temperature difference |
| $\eta_1$ | f(taxes, insurance, maintenance) |
| $\eta_2$ | f(overhead costs) |
| $\Pi$ | Product operand |
| $\rho$ | Density |
| $\Sigma$ | Summation operand |
| $\psi$ | Capital cost exponent |
| $\Omega_D$ | List of feasible alternatives |

Abbreviations

| | |
|---|---|
| CAA | Clean Air Act |
| CNF | Conjunctive normal form approach |
| CPU | Central Processing Unit |
| CSTR | Continuous stirred tank reactor |
| $CU$ | Cold utility |
| CWA | Clean Water Act |
| DNF | Disjunctive normal form approach |
| EPA | Environmental Protection Agency |
| GBD | Generalized benders decomposition |
| HEN | Heat exchanger network |
| HON | Hazardous Organic NESHAPs |
| $HU$ | Hot utility |
| *LMTD* | Logarithmic mean temperature difference |
| LB | Lower bound |
| LP | Linear programming |
| $M\&S$ | Marshall & Swift Index |
| MACT | Maximum Achievable Control Technology standards |
| MEN | Mass exchanger network |
| MILP | Mixed integer linear programming |
| MINLP | Mixed integer nonlinear programming |
| NAAQS | National Air Ambient Quality Standards |
| NESHAPs | National Emission Standards for Hazardous Air Pollutants |
| NLP | Nonlinear programming |
| $NPV$ | Net present value |
| OA | Outer approximation |
| *PFR* | Plug flow reactor |
| RCRA | Resource Conservation and Recovery Act |
| SQP | Sequential quadratic programming |
| TCA | Total Cost Assessment |
| UB | Upper bound |

| | |
|---|---|
| VOC | Volatile organic compounds |

Subscripts

| | |
|---|---|
| $alt$ | Process alternatives |
| $B$ | Base case process |
| $e$ | Existing process |
| $l$ | Liquid phase |
| $g$ | Gas phase |
| $n$ | New process |

Mathematical symbols

| | |
|---|---|
| $\vee$ | Or |
| $\wedge$ | And |
| $\varnothing$ | Null set |
| $\cup$ | Union |
| $\cap$ | Intersection |
| $\neg$ | Not |

# CHAPTER I

# INTRODUCTION

The chemical processing industry is faced with a need to manufacture quality products while minimizing production costs and complying with a variety of safety and environmental regulations. These regulations include the Clean Air Act (CAA), the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA), and the most recent the Hazardous Organic National Emission Standards for Hazardous Air Pollutants (HON) (Zanetti 1994). In 1990, the Environmental Protection Agency (EPA) promulgated the Pollution Prevention Act (Freeman, et al. 1992). This act declared that the national policy of the United States is to prevent or reduce pollution at the source, that pollution which cannot be prevented should be recycled in an environmentally safe manner, and that waste disposal should be employed only as a last resort. Hydrocarbon Processing (1993) reports on an increased rate in pollution control costs and estimates that by 1995 the hydrocarbon processing industry will spend 152.6 billion dollars in pollution control.

As a result of the Pollution Prevention Act, the constant change in regulations, and the increasing pollution control costs, and because waste treatment is not the solution to the pollution problem, end-of-the-pipe treatment is no longer feasible or recommended. Therefore, a recent approach that has been taken is to apply source reduction instead of end-of-the-pipe treatment. In this way, industry complies with all regulations and reduces waste treatment costs, thus increasing the overall profit of operation.

The EPA defines waste minimization as the reduction, to the greatest extent possible, of hazardous pollutants that are generated and subsequently treated, sorted, or disposed (Waste Minimization 1988). Waste minimization can be accomplished by retrofitting an existing process by performing minor modifications to the current process in order to increase its overall performance. An initial approach in waste minimization was aimed at good housekeeping practices, a second generation of waste minimization efforts is focused towards modifying existing processes in order to reduce emissions, and a third generation will focus on developing highly selective separation processes and more selective reaction technologies (Cohen and Allen 1992). Even though the third generation will probably generate better results towards waste minimization, it requires time and money to develop new technologies and alternative process chemistries. The present study will focus on the second and third generation for retrofitting an existing process by modifying it in order to reduce emissions and increase its overall performance.

When considering the retrofit problem, there can be several alternatives. These are in order of increasing costs (Grossmann, et al. 1987): (1) Modify the operating conditions, (2) Redefine the use of the present equipment, (3) Modify the present equipment, and (4) Add new equipment. The three basic methodologies used for retrofit design are (Gundersen 1989):

1) Hierarchical design methods: These methods consist of a series of heuristic rules to screen process alternatives.
2) Methods based on pinch technology: These methods were developed during the energy crisis for the efficient use of energy.
3) Methods based on mathematical programming: These methods rely on optimization techniques to solve the Mixed Integer Non-Linear Programming (MINLP) problem.

These methods originally emerged as grassroot design methodologies for the synthesis of new processes, but have been applied to retrofit problems. The present work based on the basic methodologies will develop a combined approach using process simulation, optimization, and economic analysis tools to formulate the problem as a Mixed Integer Non-Linear Programming (MINLP) problem (Grossmann 1989), evaluating all the possible alternatives in order to reduce the environmental impact and improve the energy consumption of an existing process.

The final decision criteria used to select a specific process alternative will rely on an economic evaluation of this alternative. The economic model used to evaluate each alternative should take into account the capital and manufacturing costs (direct production costs, fixed charges, plant overhead costs, and general expenses) associated with a specific process. This takes into consideration the fact that the most environmentally friendly process might not be the most economical. The economic tool used to compare process alternatives will be the net present value (NPV) method that represents the best profitability comparison tool (Peters and Timmerhaus 1980). When comparing different process alternatives, the optimum alternative selected will be the one that satisfies production demand with a minimum cost. This will guarantee that the company will be ahead of its competitors and secure its long term survival. This is important, as the waste minimization approach is focused not only on the manufacturing process itself, but on the product life cycle, from raw materials to final disposition (Freeman, et al. 1992).

A sensitivity analysis, together with a hierarchical method (Douglas and Stephanopoulos 1994) will be used as a starting point to identify possible alternatives and to generate the MINLP superstructure. By identifying the heat sources and heat sinks of a process, the Pinch Technology methods (Linnhoff 1994) estimate the minimum utility requirements, the number of heat exchanger units, and the heat exchanger area. Although this approach has been successful, it is a step procedure, where each step is affected by the previous one. A suggested approach (Yee and Grossmann 1990; Ciric and Floudas 1990) is to treat the heat integration as a simultaneous optimization problem formulating it as an MINLP problem.

Until recently (Diwekar and Rubin 1993), most of the work in the area of MINLP has been done with equation based simulators. For this study, the formulated problem will be solved using ASPEN PLUS™ a sequential modular simulator available to most industries, the built in models as well as the in-line FORTRAN capabilities will be used to model the process and solve the MINLP problem. In summary, the proposed methodology consist of four sections: (1) Development of base case model, (2) Generation of process retrofit alternatives, (3) Evaluation and optimization of process retrofit alternatives, and (4) Evaluation of future scenarios.

The process selected for this study is the production of methyl chloride ($CH_3Cl$ ) (Student Contest Problem 1964) by the thermal chlorination of methane. This process was selected because of its environmental impact, regulatory restrictions, and potential for improvement. Most of the methyl chloride produced (79%) is used for the manufacture of silicones, other uses include the manufacture of methyl cellulose, agricultural chemicals, quaternary amines and butyl rubber. The demand for 1991 was 785 million pounds with an estimated demand in 1996 of 845 million pounds (Chemical Profiles 1992).

Methyl chloride and the corresponding by-products methylene chloride ($CH_2Cl_2$ ), chloroform ($CHCl_3$ ), and carbon tetrachloride ($CCl_4$) are considered hazardous wastes under RCRA and are regulated by the CWA, CAA, and HON. Methylene chloride, a suspected carcinogen, chloroform, and carbon tetrachloride are also included in the 33/50 program, which is a voluntary program to reduce the emissions of specific chemicals by 33% in 1992 and by 50% in 1995 (Freeman, et al. 1992). Fugitive emissions of carbon tetrachloride need to be eliminated by the year 2000 according to the Montreal Protocol, and a ban on its production goes in effect by 1996. The Montreal Protocol is an international agreement for the cooperation on research, development, public awareness, and information exchange, to develop new technologies that will reduce the depletion of the ozone layer (Department of State Bulletin 1987). Under certain conditions (Johnson, et al. 1959) the process can yield vinyl chloride, vinylidene chloride, 1,2-dichloroethylene, ethylidene dichloride, methyl chloroform, ethylene dichloride and trichloroethylene, all of which are considered hazardous waste under RCRA.

The process consists primarily of a reactor where the reactions take place. The reactor effluent is cooled and it is washed with water to remove the hydrogen chloride (HCl) generated, the water stream contains both HCl and a small amount of chloromethanes. The chloromethanes mixture is then dried to remove the water. This drying is usually accomplished through a series of dehumidification towers containing sodium hydroxide (NaOH) and sulfuric acid ($H_2SO_4$) generating several waste streams.

The water is removed to minimize corrosion where the streams contain HCl or chlorine and to prevent the hydrolysis and decomposition of the product and by-products. As a next step part of the mixture is recycled to the reactor, and finally the mixture is compressed and passed through a series of distillation columns to separate each of the four products.

The objectives of this work are:

- Determine the advantages of applying waste minimization techniques to chemical processes, during the design and retrofit phases.
- Develop a methodology for retrofitting existing processes to minimize waste while remaining economical.
- Apply the methodology developed to an existing process for the production of methyl chloride, by incorporating environmental, economic and energy efficiency constraints.

The present work is divided into several sections:

- Overview of regulations, waste minimization techniques, and process retrofit methodologies
- General methodology
- Development of base case model
- Selection of process retrofit alternatives
- Economic analysis
- Evaluation and optimization of process alternatives
- Case study: methyl chloride process

The methyl chloride process was first modeled using ASPEN PLUS™ to determine the current operating conditions and performance. As a next step, a superstructure was generated using a sensitivity analysis and a hierarchical procedure to determine possible process alternatives. The superstructure was modeled as an MINLP problem to include all the possible process alternatives. The MINLP was solved using ASPEN PLUS™, and as a result feasible economical alternatives were identified to reduce the waste generated. The selected flowsheet was then used to formulate a superstructure to determine the optimum configuration for the heat exchanger network (HEN) and improve the energy consumption of the methyl chloride process.

# CHAPTER II

# BACKGROUND

## Regulations

The chemical processing industry has to comply in the present and in the future with several environmental regulations. These regulations are administered by the Environmental Protection Agency (EPA). Among the different regulations, these that impact this study are: (1) Clean Air Act (CAA), (2) Clean Water Act (CWA), and (3) Resource Conservation and Recovery Act (RCRA).

The CAA sets definite goals for emission reductions and air quality improvement. It establishes National Emission Standards for Hazardous Air Pollutants (NESHAP) and National Air Ambient Quality Standards (NAAQS) to protect public health and welfare. NESHAP standards have been developed (Carson and Cox 1992) for arsenic, asbestos, benzene, beryllium, mercury, radionucleides, and vinyl chloride. This list is likely to be expanded in the future. The CAA amendments of 1990 require strict control over the emission of 189 toxic air pollutants. Sources emitting 10 tons per year of any pollutant, or 25 tons per year of any combination of the listed pollutants, will be required to install Maximum Achievable Control Technology (MACT) standards (Carson and Cox 1992). These standards require the maximum emission reduction that is economically achievable. MACT standards will be promulgated by the year 2000. The most recent amendment to the CAA is the Hazardous Organic NESHAP (HON) (Federal Register 1994). The HON is aimed towards reducing, within three years, the hazardous emissions of volatile organic compounds (VOC). Companies will be required to control leaks from vents, wastewater treatment units, storage vessels, valves, pumps, and other equipment by treating them as emission points.

The goal of the CWA is to restore and maintain the chemical, physical, and biological integrity of the water. The act establishes effluent limitations for 126 toxic pollutants (Kovalic 1987).

RCRA defines hazardous waste and controls their handling and disposal. Waste is defined by the EPA as anything produced by a process or by accident, which cannot be directly used on-site as a raw material for another process without some sort of treatment or cannot be reused on-site at all (Carson and Cox 1992). A waste is considered hazardous by exhibiting one or more of the following characteristics: ignitability, corrosivity, reactivity, and toxicity. A waste is also hazardous if it is listed in a series of tables that are chemical oriented and process oriented (Code of Federal Regulations 1994). A characteristic waste can be eliminated by treatment, but a listed waste will always remain a hazardous waste. RCRA also identifies different levels of hazardous waste generators as a function of the amount of waste generated, establishing regulatory requirements for each level.

## Waste Minimization

The EPA published the Pollution Prevention Act (Freeman, et al. 1992) in 1990 declaring that the national policy of the United States is to prevent or reduce pollution at the source, that pollution which cannot be prevented should be recycled in an environmentally safe manner, and that waste disposal should be employed only as a last resort. As part of its pollution prevention strategy the EPA initiated the 33/50 program, which is a voluntary program to reduce the emissions of 17 chemicals by 33% by 1992, and by 50% by 1995.

Waste minimization is defined by the EPA (Waste Minimization 1988) as the reduction to the extent feasible, of hazardous waste that is generated or subsequently treated, stored or disposed of. Several waste minimization techniques that can be applied are shown in Figure 2.1.

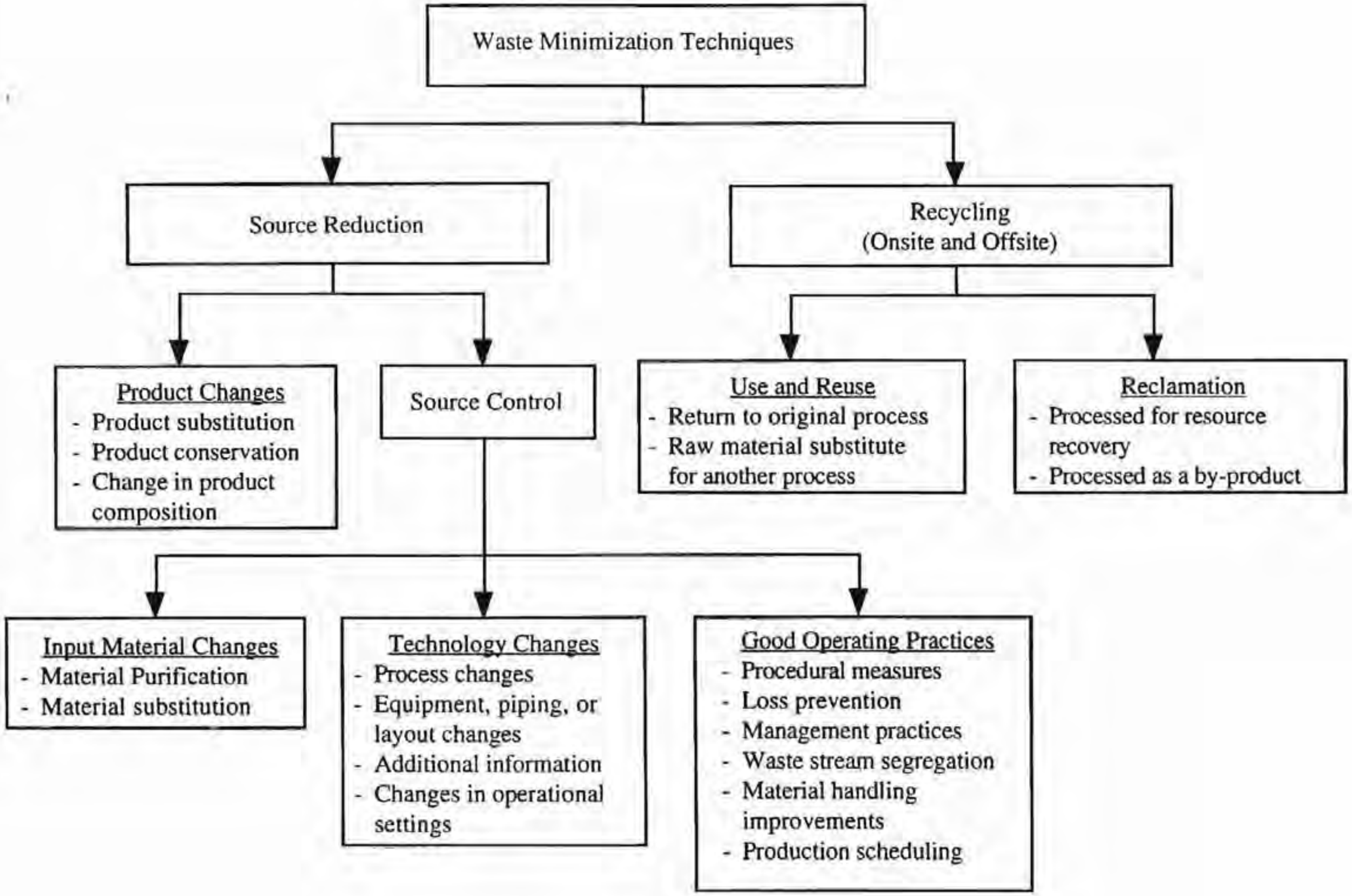

Figure 2.1: Waste minimization techniques (Waste Minimization 1988)

The waste management hierarchy defined by EPA ranks pollution prevention as a top priority. The hierarchy is: (1) source reduction, (2) recycling, (3) waste separation and concentration, (4) energy and material recovery, (5) waste treatment, and (6) waste disposal (Mizsey 1994).

An initial approach in waste minimization was aimed at good housekeeping practices, a second generation of waste minimization efforts is focused towards modifying existing process in order to reduce emissions, and a third generation will focus on developing highly selective separation processes and more selective reaction technologies (Cohen and Allen 1992). Even though the third generation will probably generate better results towards waste minimization, time and money must be invested to develop new technologies and alternative process chemistries.

As a result of the Pollution Prevention Act, the constant change in regulations, and the increasing pollution control costs (see Figure 2.2), end-of-the pipe treatment is no longer feasible or recommended. Therefore, a recent approach that has been taken is to apply source reduction instead of the end-of-the-pipe treatment. This approach has been proven to be cost effective (see Table 2.1).

## Process Retrofit Methodologies

Process retrofit can be accomplished by performing modifications to existing processes in order to increase their overall performance. There exist several alternatives to retrofit a process. These are, in order of increasing costs (Grossmann, et al. 1987): (1) Modify the operating conditions, (2) Redefine the use of the present equipment, (3) Modify the present equipment, and (4) Add new equipment. The current methodologies used for retrofit design were originally developed for the design of new processes, but have been successfully applied to retrofit problems. These process retrofit methods can be classified in three general groups (Gundersen 1989): (1) Hierarchical design methods, (2) Methods based on pinch technology, and (3) Methods based on mathematical programming.

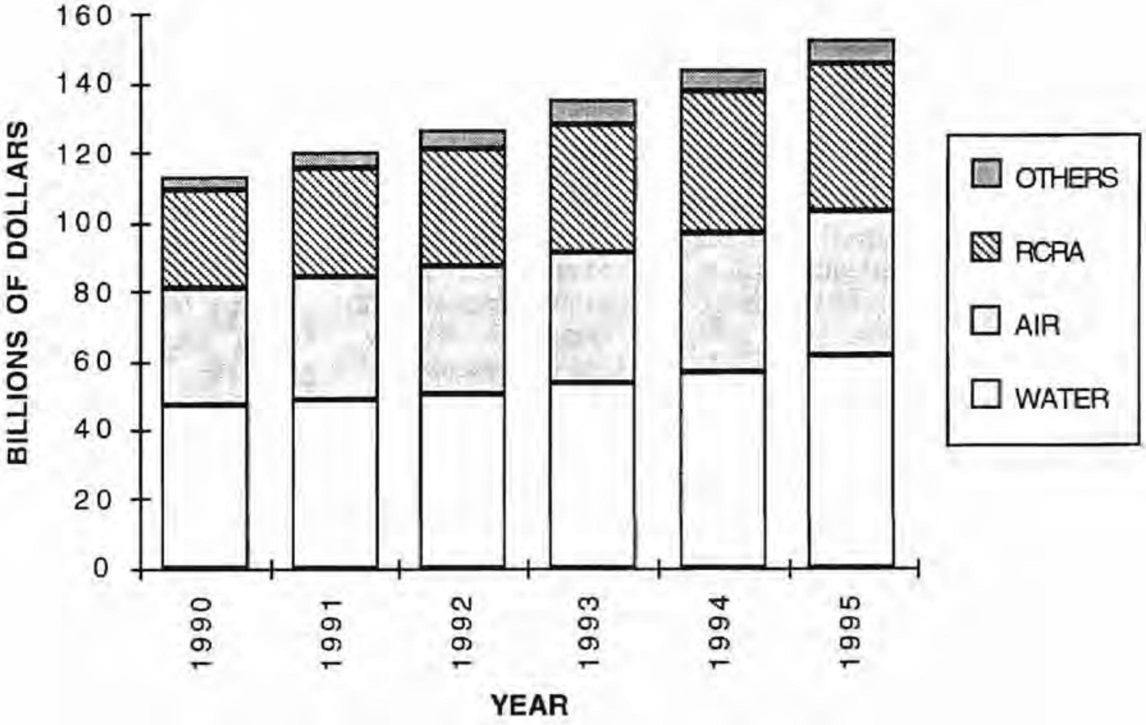

Figure 2.2: Annual pollution control costs for the hydrocarbon processing industry (Environmental Processes 1993)

Table 2.1: Waste Reduction Projects

| Company | Accomplishments |
|---|---|
| *Amoco*<br>Waste Minimization Program (1983) | Between 1983 and 1988, Amoco reduced its hazardous waste by 86%, saving the company about $50 million. |
| *Chevron*<br>Save Money and Reduce Toxics Program (SMART, 1987) | From 1987 to 1990, Chevron reduced hazardous waste by 60% and saved more than $10 million in disposal costs. |
| *Dow*<br>Waste Reduction Always Pays (WRAP, 1986) | SARA 313 overall releases are down from 12,252 tons in 1987 to 9,659 tons in 1989, a 21% reduction. Offsite transfers are down from 2,855 tons (1987) to 2,422 tons (1989), a reduction of 15%. Air emissions for 1989 showed a 54% decrease from 1984 |
| *General Dynamics*<br>Zero Discharge (1985) | Nearly 40 mill. lb. of hazardous waste discharge eliminated from 1984 to 88 (approx. 72%). Sales increased from $7.3 to 9.35 billion over the same period. |
| *IBM* | Hazardous waste generation was reduced 38% from 1984 to 88; 84% of IBM's hazardous waste was recycled in 1988; 28% of all solid waste from IBM US operations was recycled in 1988; IBM U.S. emissions were reduced 20% from 1987 to 88; and, IBM U.S. had a decrease of 25% in its CFC emissions between 1987 and 88. |
| *Monsanto*<br>Priority One (TRI wastes) | From 1987 to 1990, Monsanto achieved a 39% reduction in hazardous air emissions. |
| *Speciality Adhesives and Chemicals* | An analysis of an amine production process increased the conversion reducing the waste in 95 tons/yr. By considering the recycling of excess reactant an additional waste reduction of 70 tons/yr and a decrease of 20% of manufacturing costs was obtained. |

Source: Benforado and Ridlehoover (1991); Freeman (1992); Morris and Robertson (1993); Thayer (1992); Woodman (1989).

### *Hierarchical Design Methods*

The hierarchical approach suggested by Douglas (1987) combines the use of cost diagrams to identify process retrofit alternatives and a series of heuristic rules to screen the alternatives identified. These heuristic rules are presented in a hierarchical order (see Table 2.2). This method is not very rigorous, but gives a starting point for the generation of feasible alternatives that can be further analyzed with more rigorous techniques.

Table 2.2: Hierarchical Procedure

| Level | Description |
|---|---|
| Level 0 | Input information |
| Level 1 | Number of plants |
| Level 2 | Input-output structure of flowsheet |
| Level 3 | Recycle structure |
| Level 4 | Separation system |
| Level 5 | Energy integration |
| Level 6 | Evaluation of alternatives |
| Level 7 | Flexibility and control |
| Level 8 | Safety |

Source: Douglas and Stephanopoulos (1994)

### *Methods Based on Pinch Technology*

These methods were developed during the energy crisis for the efficient use of energy (Linnhoff 1994). The basic principle behind pinch technology, also known as heat integration, is to maximize the heat transfer between process streams, and minimize the utility requirements. Through the use of a thermodynamic analysis and the establishment of a minimum temperature difference $\Delta T_{min}$, the minimum utilities are calculated by constructing a composite curve. A grid diagram is used to determine the distribution of the heat exchanger network (HEN), followed by an optimization of the area required. The problem with this approach is that it is a step procedure, where each step is influenced by the previous stage. A suggested approach is to treat the heat integration as a simultaneous optimization problem (Ciric and Floudas 1990; Yee, et al. 1990).

The concept of pinch technology has also been used to identify the optimum configuration of mass exchanger networks (MEN) (El-Halwagi and Manousiouthakis 1989). This method defines a set of rich and lean streams and provides a tool to improve separation systems, thus increasing the flexibility of applying reuse and recycle techniques to the process. Since the present study will focus primarily on source reduction the use of MEN will not be considered, but their use should be considered in future research.

### *Methods Based on Mathematical Programming*

The use of these methods have seen an increase over the past few years due to the advances in algorithms, computers, and software. These methods rely on optimization techniques to solve the Mixed Integer Non-Linear Programming (MINLP) problem (see Equation 2.1).

$$
\begin{aligned}
&\min_{x,y} c(x,y) \\
&s.t. \quad h(x,y) = 0 \\
&\qquad\quad g(x,y) \le 0 \qquad\qquad (2.1) \\
&y \in \{0,1\}^m \quad , \quad \mathrm{x} \in \mathrm{R}^n
\end{aligned}
$$

The problem is solved by varying the continuous variables $x$ such as temperature, pressure, and flowrate; and the discrete variables $y$ that denote the existence of a specific unit. The variables are varied in order to minimize the objective function $c$ subject to a set of equality constraints $h$ and a set of inequality constraints $g$.

The mathematical programming methods can be divided in three general groups (Gundersen-1989): (1) Branch and bound, (2) Generalized benders decomposition, and (3) Outer approximation.

1) Branch and bound : This method is based on relaxing the integrality requirements of the discrete variables. A tree evaluation of the different possibilities is performed solving a non-linear programming problem (NLP) at each node. The main advantages of this method is that it is easy to implement and strict convexity is not required. A drawback of this method is that it requires the solution of a large number of NLP subproblems.

2) Generalized benders decomposition (GBD) (Geoffrion 1972): The main algorithm for this method is divided in two sections (see Figure 2.3), the NLP section has the role of predicting and upper bound and the master problem has the role of predicting a lower bound and new values for the discrete variables. This method requires fewer iterations than the branch and bound.

3) Outer approximation (OA) (Duran and Grossmann 1986): The algorithm for this method is similar to the GBD (see Figure 2.3). The main difference lies in the master problem formulation. For the OA the master problems contains both continuous and discrete variables, whereas the GBD contains only discrete variables. This method provides a better approximation of the MINLP problem, thus requiring fewer iterations than GBD. For the case of the GBD and OA, the problems gets bigger after each iteration, becoming computationally intensive. Both methods also require strict convexity.

To overcome the different drawbacks of the OA algorithm, several modifications have been proposed (Diwekar and Rubin 1993; Kocis and Grossmann 1987; Kocis and Grossmann 1989; Quesada and Grossmann 1992; Raman and Grossmann 1992; Raman and Grossmann 1993; Viswanathan and Grossmann 1989). Until recently (Diwekar and Rubin 1993) most of the work in MINLP has been done using equation based simulators. The present work will focus on applying MINLP techniques to a sequential modular simulator such as ASPEN PLUS™.

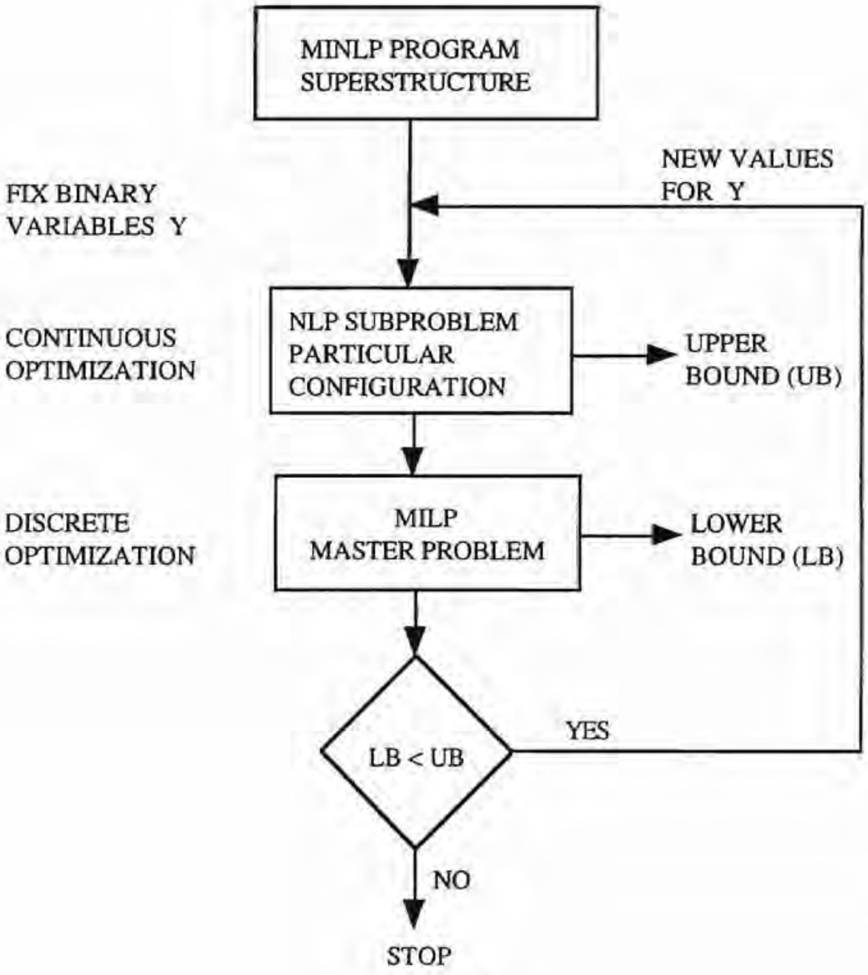

Figure 2.3

Main steps of GBD and OA algorithm (Grossmann 1989)

## Economic Analysis

The final decision criteria used to select a specific process alternative will rely on an economic evaluation of this alternative. The different alternatives should be compared against the base case with an economic model to evaluate their feasibility. The economic model used to evaluate each alternative should take into account the capital and manufacturing costs associated with a specific process. This takes into consideration the fact that the most environmentally friendly process might not be the most economical. For the retrofit scenario we should also take into account the market value of the equipment being replaced as well as the cost required to remove it.

When dealing with waste minimization projects, the economic analysis is critical in identifying the feasible alternatives. Total Cost Assessment (TCA) (Freeman, et al. 1992) provides a way to analyze the different waste related costs: usual costs (equipment, labor, and materials), hidden costs (compliance and permits), liability costs (penalties/fines and future liabilities), and less tangible costs (consumer responses and employee relations). There is no model currently available in the literature that includes all the previous information.

## Process Modeling

Process modeling through computer simulation is becoming one of the most powerful tools in process design (Fouhy 1991), providing a fast and economic way to evaluate process alternatives. Process simulators have been applied in the different phases involved in a project such as process synthesis, process design, control system design, plant startup, and plant operation (Glasscock and Hale 1994). The computer simulation packages available (Grinthal 1993) such as ASPEN PLUS™, HYSIM™, SPEEDUP™, and PROII™ have been proven to be successful in simulating chemical processes, both dynamic and steady-state.

This chapter presented a background on regulations, waste minimization, process retrofit methodologies, economic analysis, and process modeling. Based on the background, the next chapter will present a general description of the proposed methodology followed by a detailed description of each step.

# CHAPTER III

# GENERAL METHODOLOGY

This chapter presents the development of a general methodology to be applied to retrofitting existing processes. A similar methodology can also be applied for the design of new processes. The proposed methodology consists of four general steps:

1. Development of a base case model.
2. Generation of process retrofit alternatives.
3. Evaluation and optimization of process retrofit alternatives.
4. Evaluation of future scenarios.

A diagram of the proposed methodology is presented in Figure 3.1.

## Development of Base Case Model

The modification of a process requires the existence of an incentive. This incentive can be economical, environmental, quality oriented, safety improvement, etc. In order to evaluate the feasibility of each of the process alternatives, a comparison with the existing process is required. Therefore is important to have a model that accurately represents the performance of the existing process.

The development of an accurate model requires the gathering of process information. Some of this information is outlined in Table 3.1. This information requires an in depth analysis of the process. Once the information is acquired a model can be constructed. For this study, the ASPEN PLUS™ (Aspen Technology 1988) process simulator was used as the modeling tool.

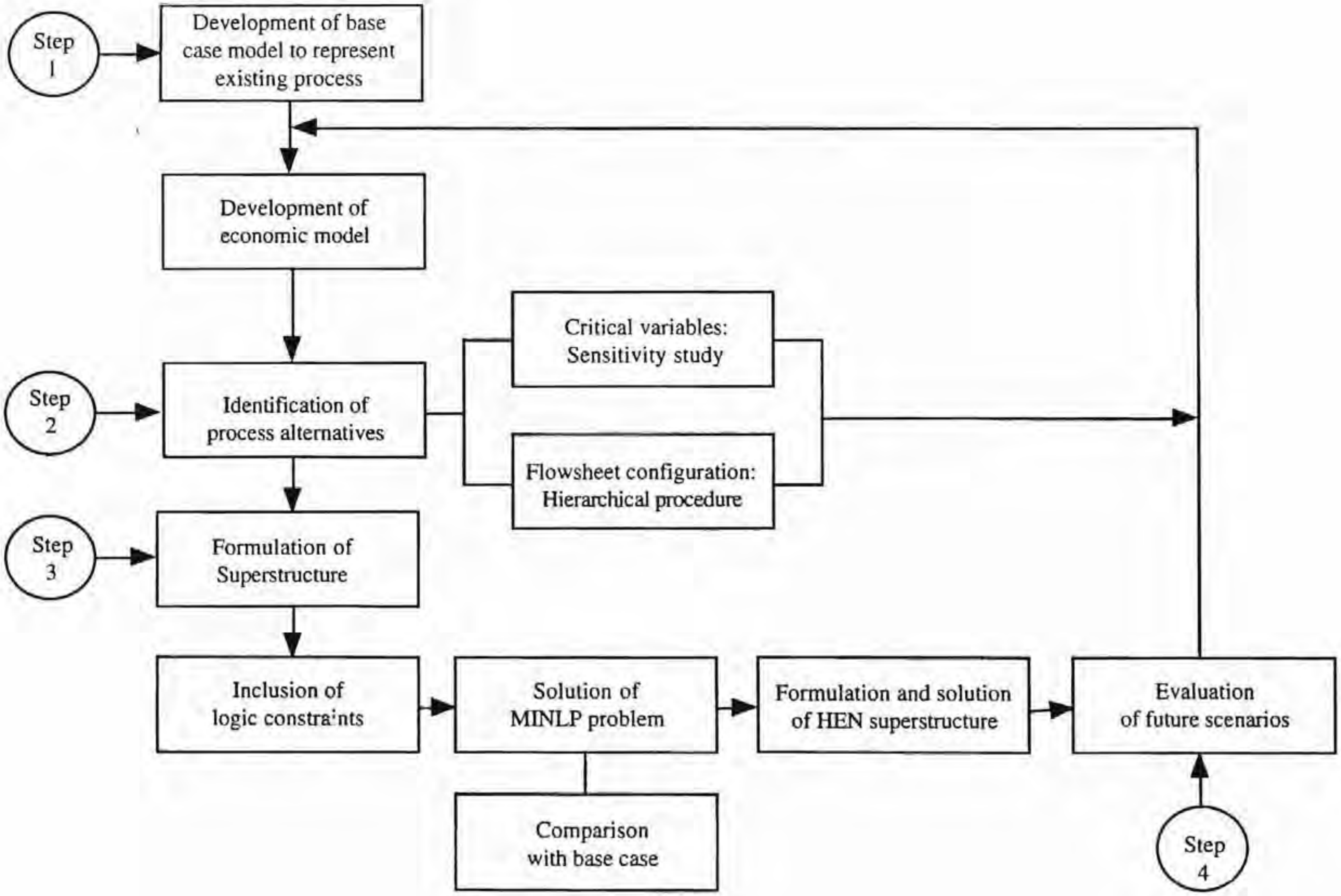

Figure 3.1: General Methodology

Table 3.1: Base-case information

a. Reaction system  
b. Kinetic data  
c. Raw materials and by-products  
d. Waste streams  
e. Process configuration  
g. Process variables  
h. Process constraints  
i. Equipment characteristics  
j. Plant Utilities

### Generation of Process Retrofit Alternatives

The development of the process alternatives is divided in two levels:

1. Zero investment level: At this level only the modification of operating parameters is considered, such as temperature, pressure, and flowrate. Thus, the process alternatives identified at this level do not require a major capital investment. The alternatives are identified through a sensitivity analysis where the effect of each variable is compared to the performance of the base case.
2. Variable investment level: In this level, different flowsheet configurations are considered through the structure modification of the existing process by rearranging the existing units or the acquisition of new ones. The alternatives in this level are identified with the use of a hierarchical procedure.

The number of alternatives identified will affect the size and complexity of the MINLP problem. Therefore, a detailed economic analysis is made to determine only the feasible alternatives, thus reducing the size of the MINLP problem.

### Evaluation and Optimization of Process Alternatives

The alternatives identified are compared against the base case by using an economic model that includes cost data for the base case and for each alternative. The economic model includes both information regarding operating conditions and capital investments. Capital and operating costs are included in order to consider that the best process to minimize waste, may not be the most economical.

The economic model is used together with all of the alternatives to generate a superstructure. An example of a superstructure is presented in Figure 3.2, where the blocks $Y_i$ represent the existance of a specific process unit and the $Z_i$ blocks represent mixer and splitter blocks. This superstructure is formulated as an MINLP problem (see Equation 2.1). Logic constraints are incorporated in the MINLP formulation (Raman and Grossmann 1993) to reduce the number of possible combinations which leads to a smaller problem.

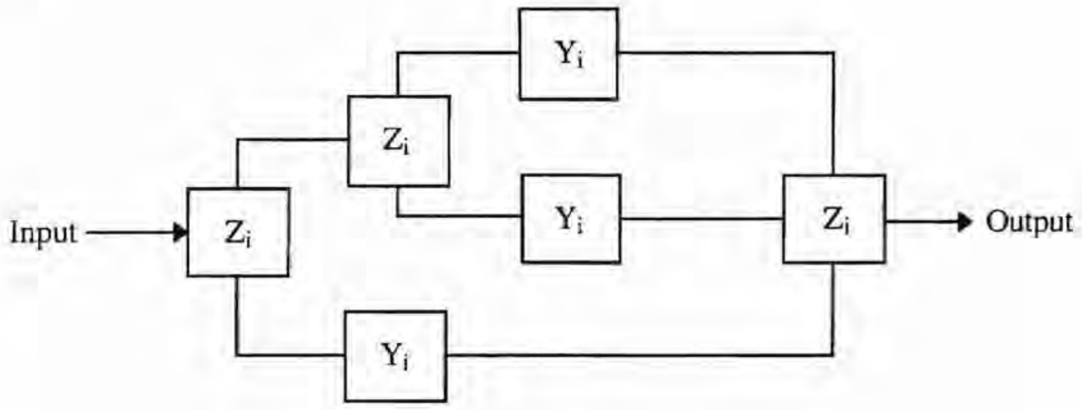

Figure 3.2: MINLP Superstructure

The solution of the superstructure gives the optimum flowsheet configuration and operating parameters in order to maximize the profit of the process. This optimum considers environmental criteria and investments costs. As a next step, a heat integration analysis is performed with the optimum flowsheet by formulating a superstructure that considers all the possible heat exchanger network (HEN) configurations, thus maximizing the internal process heat transfer and minimizing the external utilities heat requirements.

The correct approach for the heat integration analysis should be to consider the HEN together with the initial superstructure representation. Due to the size of the problem the optimization was done in a sequential analysis. This method does not explicitly consider the capital costs for heat exchangers during the initial superstructure analysis, but a good estimate can be assumed since this costs are a function of the utility requirements of each process alternative.

## Evaluation of Future Scenarios

A final analysis is performed to evaluate the flexibility of the optimum process. This analysis will determine the possible effect that any future changes in our current constraints such as product demand, environmental regulations, economic data, etc., will have on the process performance.

This chapter presented a general description of the proposed methodology. This methodology consists of four principal steps: (1) Development of base case model, (2) Generation of process retrofit alternatives, (3) Evaluation and optimization of process retrofit alternatives, and (4) Evaluation of future scenarios.

The next chapter presents the construction of the economic model that will serve as a tool to perform an initial screening of the retrofit alternatives. The economic model will then be used as the tool to do a rigorous analysis of these alternatives, and select the optimum flowsheet configuration.

# CHAPTER IV

# ECONOMIC ANALYSIS

The modification of an existing process usually requires an economic incentive. This incentive is identified through an economic model, which serves as a tool to adequately analyze the economics of the base case process and of the several retrofit alternatives.

## Economic analysis approach

The costs associated with a specific process can be divided into capital costs and manufacturing costs. The manufacturing costs are generally divided into four general subdivisions: (1) Direct production costs, (2) Fixed charges, (3) Plant overhead costs, and (4) General expenses, where the last three are considered independent of process throughput. Two major problems exist when incorporating pollution control and abatement costs in the economic analysis (see Table 4.1). The first problem is given by the fact that pollution control and abatement costs are generally considered as part of the plant overhead costs (Perry and Green 1984). This represents a major flaw in a waste reduction analysis. To overcome this flaw, it is necessary that the different waste streams associated with each process be taken as a part of the direct production costs.

A second problem arises due to the difficulty of identifying waste related costs because of their constant increase which is estimated to be 20-30% annually (LaGrega, et al. 1994). The waste related costs are a function of the characteristics of the specific waste, of the treatment options and their efficiency, and of the disposal options. Dyer and Mulholland (1994) present an economic analysis of the different pollution control technologies as a function of the waste gas flow and of the inlet and outlet concentrations.

Kuhre (1994) presents estimates for different hidden costs being a function of the hazardous characteristic of the waste and of the flowrate. Turner (1994) presents a model that incorporates several hidden costs such as transportation, disposal, training, emergency equipment and planning, handling, etc. The Multi-Option Model (Karam, et al. 1988) is a computerized hazardous waste management tool that is designed to assist generators and state officials in the analysis of hazardous waste reduction, reuse, and treatment analysis. EnviroCAD (Petrides, et al. 1994) is a similar tool that recommends alternatives for waste recovery and recycling, and if such alternatives are not useful, it recommends alternatives for treatment and disposal. These alternatives are further analyzed and evaluated.

Table 4.1: Waste related costs

I. Usual costs
    a. Equipment
    b. Labor
    c. Materials
    d. Utilities
II. Hidden costs
    a. Compliance
    b. Permits
III. Liability costs
    a. Penalties/fines
    b. Future liabilities
IV. Less tangible costs

Source: Freeman (1992)

## Economic Model

The economic performance of the base case model is used as the evaluation criteria to analyze each process alternative. The economic performance is evaluated in terms of profitability. Profitability is a function of both capital and manufacturing costs. Since the base case represents the existing process in operation, it does not consider capital cost investment. Therefore, the economic performance for the base case is a function only of income and manufacturing costs (see Equation 4.1).

$$Ep = In_B - Mc_B \tag{4.1}$$

where:

$B$ = Base case
$Mc$ = Manufacturing costs (\$/yr)
$In$ = Income (\$/yr)

The income term $In_B$ in Equation 4.1 considers revenue obtained from the product and byproducts. The byproducts obtained in a process may in some cases be considered as a revenue, but this might change in the future. To overcome this uncertainty, the byproducts are not be used as a source of revenue.

The alternatives to be considered will be evaluated in terms of their compliance with specified product demand. By fixing the specified product demand the income term in Equation 4.1 is eliminated. Therefore, the economic potential is a function only of the manufacturing costs (see Equation 4.2).

$$Mc_B = Rw_B + W_B + O_B + Ac_B \tag{4.2}$$

where:

$Rw$= Raw materials cost (\$/yr)
$W$ = Waste costs (\$/yr)
$O$ = Operating costs (\$/yr)
$Ac$ = Additional costs (\$/yr)

Based on Equation 4.2, the best alternative will be the one that satisfies production demand and requires the least amount of manufacturing costs.

The waste cost component in Equation 4.2 corresponds to the costs associated with the final disposition of the waste leaving the process. All waste treatment costs are considered to be part of the operating costs (see Equation 4.3),

$$O = \sum_{i=1}^{Y} (utility\ consumption_i)(utility\ cost)_i \tag{4.3}$$

where:

$Y$ = Total number of units

and can be modeled as part of the flowsheet. By using this approach we can follow the EPA's preferred hazardous management strategy by shifting the objective function towards waste reduction and away from waste disposal. An initial guess of the waste related costs can be assigned by considering a 2 to 1 ratio of the waste cost and the limiting reactant cost. This rule represents only an estimate that enables the objective function to be penalized for waste generation. When there is appropriate data, this rule can be represented with a more accurate representation.

## Economic Model for Process Alternatives

The process alternatives are compared against the economic performance of the base case. The optimum alternative will be the one that satisfies production demand with a minimum cost. The economic model used to evaluate the alternatives contains both capital and manufacturing costs. The capital and manufacturing costs are included in order to consider that the most environmentally friendly process might not be the most economical. To adequately compare the alternatives the Net Present Value (NPV) method represents the best profitability comparison tool (Peters and Timmerhaus 1991). Based on the NPV method, considering the salvage value as zero, and rearranging terms, the economic model applied is presented in Equation 4.4.

$$NPV = \sum_{j=1}^{ny} \left[ f_D \left( \Delta Mc(1 - Tx) + CF * D_j * Tx \right) \right] - CF \tag{4.4}$$

where:

NPV = net present value

$ny$ = number of years

$f_D$ = discount factor

$Tx =$ Tax rate

$CF =$ Fixed capital cost

$D_f =$ Depreciation factor

The term $\Delta Mc$ in Equation 4.4 represents the savings in operating costs that are obtained with a specific retrofit alternative when compared to the base case (see Equation 4.5).

$$\Delta Mc = Mc_B - Mc_{alt} \tag{4.5}$$

where:

$alt =$ process alternative

The discount factor $f_D$ in Equation 4.4, considers the cost of capital at an interest rate $i$ (see Equation 4.6).

$$f_D = \frac{1}{(1+i)^j} \tag{4.6}$$

The cost of capital will determine if the company will make a greater profit with the project or with the capital itself (Peters and Timmerhaus 1991). A suggested value for the interest rate is 15% (Peters and Timmerhaus 1991).

The depreciation factor $D_f$ in Equation 3, is estimated using the sum-of-the-years-digits method (Peters and Timmerhaus 1991) (see Equation 4.7).

$$D_f = \frac{2(ny - j + 1)}{ny(ny+1)} \tag{4.7}$$

The economic model has three variables that can be modified as required: the tax rate $Tx$, the interest rate $i$, and the number of years $ny$.

The required operating and capital costs (see Table 4.2) need to be identified for each alternative and incorporated in the economic model.

Table 4.2: Fixed capital investment items

Direct capital costs

1. Purchased equipment
2. Purchased equipment installation
3. Instrumentation and controls
4. Piping
5. Electrical equipment and materials
6. Buildings (including services)
7. Yard improvements
8. Services facilities
9. Land

Indirect capital costs

1. Engineering and supervision
2. Construction expenses
3. Contractor's fee
4. Contingency

Source: Peters and Timmerhaus (1991)

There exist several types of estimates that can be used to determine the required capital investment. The use of cost indexes (see Equation 4.8),

$$Present\ cost\ =\ original\ cost\left(\frac{index\ value\ at\ present\ time}{index\ value\ at\ time\ of\ original\ cost}\right) \qquad (4.8)$$

such as the Marshall and Swift Equipment Cost Index, and the Chemical Engineering Plant Cost Index (Peters and Timmerhaus 1991), can be helpful when capital cost information is available from some time in the past. An alternative method is to estimate the costs by scaling, if the new unit is similar to one of another capacity for which cost data is available (see Equation 4.9).

$$CF_n = CF_e\left(\frac{Q_{v_n}}{Q_{v_e}}\right)^{\psi} \tag{4.9}$$

where:

$Q_v$ = Plant or equipment capacity

$CF$ = Fixed capital cost

$e$ = Existing process

$n$ = New process

$\psi$ = Exponent ≈ 0.6 - 0.7

A similar relationship can be used for the case of operating costs (see Equation 4.10) (Holland, et al. 1974).

$$\frac{Ap_n}{f_n} = \frac{1}{f_n}\left[\eta_1 CF_e\left(\frac{f_n}{f_e}\right)^{0.7} + \eta_2 C_L No\left(\frac{f_n}{f_e}\right)^{0.5} + Au_e\left(\frac{f_n}{f_e}\right)\right] \tag{4.10}$$

where:

$Ap$ = Annual operating costs

$Au$ = Annual cost of utilities

$f$ = Flowrate (lb/yr)

$C_L$ = Shift earning per hour

$No$ = Number of operators

$\eta_1$ = f(taxes, insurance, maintenance) ≈ 0.09

$\eta_2$ = f(overhead costs) ≈13500

Peters and Timmerhaus (1991) present several correlations that can be used to estimate the capital costs of a great variety of process equipment. ASPEN PLUS™ includes a cost estimation block that can be used to estimate the fixed capital costs. The choice of any particular method to estimate capital and operating costs will depend upon the amount of information available and the accuracy desired.

The economic model will be evaluated in an annual basis consisting of 8150 hr/yr for continuous processes or 7500 hr/yr for batch processes (Douglas 1988). The economic model (see Equation 4.4) is used for an initial screening of process retrofit alternatives, and as the objective function to be maximized by an optimization algorithm.

This chapter presented the development of the economic model. This model includes information regarding product and byproduct revenue, raw material costs, waste related costs, utility costs, and equipment costs. This model will be used in the next chapter to do an initial screening of the possible alternatives. It will then be used as the objective function in the optimization subroutine.

# CHAPTER V

# SELECTION OF PROCESS RETROFIT ALTERNATIVES

This chapter presents the development of a process model to represent the current performance of the process. This mathematical model can be constructed using several process simulators. Once this model is constructed it can be used to identify feasible alternatives to be further evaluated and optimized.

## Base Case Process Model

The base case process model is required to evaluate the current performance of the process, serving as a guideline to analyze the different retrofit alternatives. The process model will function as an inexpensive experimental tool that will allow us to evaluate the economic and environmental effect that the various process alternatives will have in the performance of our process. Some of the information required for the development of the base case model was presented in Table 3.1.

An important factor in the development of the base case process model is to determine its scope, by identifying the units and operations to be included. The more units included will make the model more accurate but also will make it more computationally intensive. For the case of waste minimization projects, it is necessary to include all the units that are point sources for each waste stream in the process. The process model should also include operations and units that have an important economic impact in the process, such as compressors.

## Process Modeling Tool

The process simulator used for this study is ASPEN PLUS™ developed by ASPEN Technology Inc. (ASPEN Technology 1988). Among the different tools incorporated in ASPEN PLUS™, Model Manager is a user friendly tool that guides the user during the input of the necessary modeling parameters. ASPEN PLUS™ includes several data banks for component properties, a wide range of equations of state, different reactor blocks, and several unit operations such as distillation columns, absorbers, heat exchangers, etc. It has the capability of performing rating calculations as well as rigorous simulation; and has also the feasibility of incorporating user developed FORTRAN blocks. ASPEN PLUS™ has been successfully applied to process simulation (Diwekar, et al. 1992a; Dokurno and Douglas 1984; Farag, et al. 1992).

## Process Retrofit Alternatives

There are two levels of possible alternatives: (1) The zero investment level and (2) the variable investment level. The zero investment level considers the modification of existing operating parameters such as temperature, pressure, and flowrate. Thus, requiring no major capital investments. The variables to be modified are identified through a sensitivity analysis where their effect is compared against the performance of the base case operation.

The second level of alternatives also referred to as the variable investment level considers different flowsheet configurations through the structure modification of the existing process by rearranging the existing units or the acquisition of new ones. The alternatives in this level are identified through the use of a hierarchical procedure. Based on the procedure proposed by Douglas and Stephanopoulos (1994), the applied procedure consists of four principal steps (see Table 5.1).

Table 5.1: Hierarchical Procedure - Zero Investment Level

Level 1: Input information
  - Chemistry
  - Reaction conditions
  - Product rate and product purity
  - Processing constraints
  - Raw materials
  - Regulations (environmental, health, and safety)
  - Wastes and byproducts
  - Plant site data

Level 2: Input - output structure of flowsheet
  - Raw material purification
  - Recycle and purge streams
  - Recovery of byproducts

Level 3: Recycle structure
  - Reactor systems
  - Recycle streams

Level 4: Separation system
  - Separation system synthesis
  - Vapor recovery system
  - Liquid recovery system
  - Solid recovery and separation system

Source: Douglas (1992)

When applying the hierarchical procedure, it is important to consider waste minimization options at each level. These options should be addressed as multimedia pollution prevention strategies, where the waste is eliminated, not changed from one media to another media. Chadha (1994) lists 100 pollution prevention strategies based on (1) engineering design, (2) process chemistry and technology, (3) operating procedures, and (4) maintenance practices.

The number of alternatives identified in each investment level will affect the size and complexity of the MINLP problem, therefore an economic comparison of each alternative against the base case is made to determine the feasible alternatives.

This chapter presented the development of the base case process model to represent the current performance. This model was used to identify the possible process alternatives to be further evaluated and optimized. The selection of alternatives was accomplished using a two level approach that considers changes in operating conditions, equipment, and flowsheet configurations. The next chapter presents the development of the superstructure using the alternatives identified in the present chapter.

# CHAPTER VI

# EVALUATION AND OPTIMIZATION OF PROCESS RETROFIT ALTERNATIVES

This chapter will present the method used to evaluate the previously defined process alternatives and select the best alternative by solving a MINLP problem. The alternatives identified together with the objective function are used to generate a superstructure to evaluate using a MINLP procedure and to select the optimum flowsheet configuration. The optimum flowsheet is used to generate a new superstructure that incorporates all the possible heat exchanger network (HEN) configurations. This superstructure is evaluated using MINLP and the optimum HEN configuration is selected.

## Formulation of Superstructure

The base case and all of the retrofit alternatives are used to formulate an overall flowsheet superstructure (see Figure 6.1). The objective function in Equation 2.1 is formulated using the economic model (see Equation 4.4). The continuous variables $x$ are identified through the sensitivity analysis, and the discrete variables $y$ that represent the existence of a specific unit are identified through the hierarchical procedure. The discrete variables were defined using ASPEN PLUS™ FSPLIT blocks by varying the flow fraction between 0 and 1. Due to the black box characteristic of ASPEN PLUS™, most of the constraints $h(x,y)$ and $g(x,y)$, are already built into the flowsheet model.

The formulation of a superstructure that includes all possible alternatives, can initially be considered as a more complicated task. This idea can be refuted by the fact that optimizing a section of the superstructure (suboptimization) provides a technique for approaching an optimum, but does not necessarily ensure that an overall optimum has been obtained (Edgar and Himmelblau 1988). In addition, by formulating the whole superstructure as one problem we may in fact reduce the size of the model to be evaluated. The model for each of the sections in Figure 6.1 will contain a total of 3 processing units, for a total of 9 processing units. By using a superstructure representation, we take advantage of the similar units, reducing the model to only 6 processing units. For such a small superstructure presented in Figure 6.1, this reduction might not be significant, but as the superstructure gets bigger, it will have an important effect on the optimization of the system.

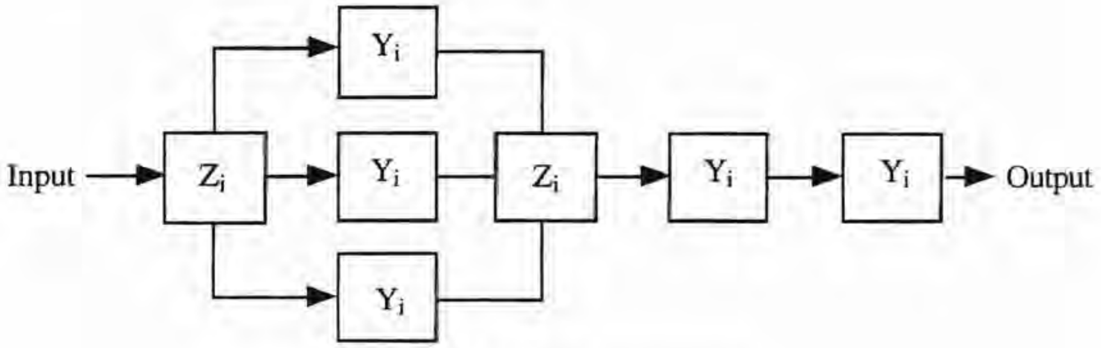

Figure 6.1: MINLP Superstructure

The Sequential Quadratic Programming (SQP) method built in ASPEN PLUS™ was used as the optimization algorithm. Other than the specific optimization subroutine that is used in the evaluation of the superstructure, two factors are critical in order to obtain an optimum solution: (1) A feasible search region, and, (2) An initial starting point. The feasible search region will determine the boundaries of the solution. As can be seen in Figure 6.2 a nonlinear function can present two or more extremum (Edgar and Himmelblau 1988). Depending on the search region selected $a<x<b$ or $b<x<c$ the optimization subroutine may identify a local optimum *d* or a global optimum *e*. Therefore, it is important to be aware that the boundaries selected will enclose the local optimum but not necessarily the global one. These boundaries are generally fixed by physical constraints or can be determined through several case studies. The distinction between a local optimum

and a global optimum becomes important when dealing with nonlinear optimization (Edgar and Himmelblau 1988). The concave or convex behavior of the objective function will help establish whether a local optimum is also the global optimum (Edgar and Himmelblau 1988).

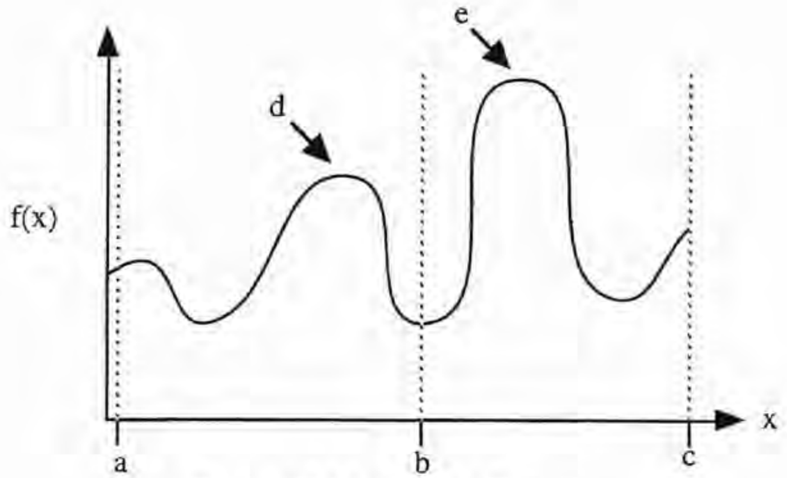

Figure 6.2 Multimodal Function

A good initial starting point is required to guarantee that the result obtained represents a true optimum and to reduce the number of iterations. The closer the initial guess is to the optimum, the faster the optimization subroutine will converge. The results obtained from the base case simulation and from the simulation of each alternative is used as the initial guess for the optimization subroutine. The identified variables are then varied between the selected ranges until an optimum answer is found.

The MINLP subroutine considers the possibility of having zero flows to specific operating units within the flowsheet. This is to simulate a particular part of the flowsheet being ignored. To adequately handle the zero flows with ASPEN PLUS™, the tear streams used to converge the flowsheet should only use the material flow as a convergence variable, and should not use the default state variables of pressure and enthalpy. The use of such variables will cause convergence problems for the optimization block. The objective function sampling variables such as heat duties, power requirements, and cost variables need to be initialized to prevent FORTRAN errors that occur due to zero flow calculations. The initialization is done using a FORTRAN block as the first step in the computational sequence. For the case of heat exchanger duties, these need to be initialized as part of the objective function.

Logic constraints are incorporated into the MINLP problem to reduce the number of alternatives to evaluate. The superstructure is simplified by representing the splitter and mixer units as Z blocks and the other units by Y blocks. The logic constraints are then formulated by using Boolean decision variables and the logic representation of the superstructure (Raman and Grossmann 1992).

## MINLP Algorithm

The algorithms for solving MINLP problems can be divided in three general classifications: (1) Branch and bound, (2) Generalized benders decomposition, and (3) Outer approximation. The literature reports various modifications to each of these categories as a general method is being developed. Quesada and Grossmann (1992) proposed an LP/NLP based branch and bound algorithm that is aimed at the solution of MINLP problems in which the bottleneck lies in the combinatorial search of the 0-1 variables. This method may be combined with the outer approximation algorithm where the nonlinear functions are linearized. Due to the black box characteristic of ASPEN PLUS™, the nonlinear constraints are unknown. Current research is being done to develop a code to be used with ASPEN public version to generate these approximations by using pseudo variables, and provide a solution for the MINLP problem (Diwekar 1994). The use of approximations provide a better representation of the MINLP problem and will generally provide the solution in fewer iterations. For this study no approximations were included in the algorithm, and will be considered as a next step in future research.

The algorithm employed based on the LP/NLP based branch and bound algorithm was modified to include a disjunctive normal form approach (DNF) (Raman and Grossmann. 1993). The DNF approach is useful in cases when the number of feasible alternatives is significantly smaller than the number of 0-1 combinations. However if the number of feasible alternatives is large, the conjunctive normal form approach (CNF) is used. Both approaches consist of applying the branching rule and the logical chaining. The branching rule is used to determine the next variable to be branched in the solution tree in order to search among branches that will lead to integer solutions as soon as possible. The logical chaining approach attempts to fix as many of the other binary variables as possible by analyzing the logic representation of the superstructure. The algorithm to solve Equation 2.1 consists of 8 steps:

Step 0: Initialization step

This step initializes all the variables required for the algorithm. The upper bound to the solution is set to infinity (see Equation 6.1),

$$Z^u = \infty \tag{6.1}$$

where

$Z^u$ = upper bound to the solution

the list of open nodes that contains the nodes to be evaluated is initialized as an empty set (see Equation 6.2),

$$P = \varnothing \tag{6.2}$$

where

$P$ = list of open nodes

and the initial set of the integer variables $y^i$ is fixed. The initial set selected should provide a good estimate of the expected optimum value to reduce the number of nodes to evaluate. For the methodology proposed the initial set corresponds to the base case process.

Step 1: This step consists in the solution of the initial nonlinear programming (NLP) subproblem, that corresponds to the optimization of the base case. The solution of the initial set is done with the ASPEN PLUS™ optimization block, and provides an upper bound to the problem. If the solution of the NLP is infeasible, the upper bound to the solution is set to infinity (see Equation 6.1).

Step 2: The integrality requirements of the set of discrete variables $y$ are relaxed (see Equation 6.3).

$$y_i \in \{0,1\} \quad \Rightarrow \quad y_i \geq 0 \ \text{ and } \ y_i \leq 1 \tag{6.3}$$

The problem containing the relaxed integer variables is solved using the ASPEN PLUS™ optimization block. This provides a lower bound to the problem. The vector $P_1^0$ containing the results from the discrete variables is stored in the list open nodes (see Equation 6.4).

$$P = P \cup P_1^0 \tag{6.4}$$

If the solution to the problem provides an integer value for the discrete variables go to step 6.

Step 3: The list of open nodes can be represented by a tree, where each variable to be evaluated is represented by a branch (see Figure 6.3). This list may contain several discrete variables.

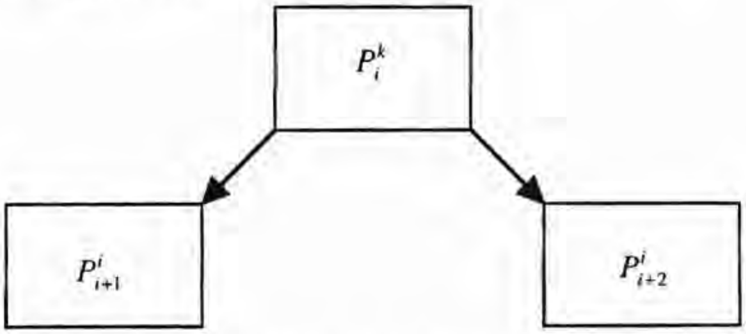

Figure 6.3: Tree of variables to be evaluated

In order to search among branches that will lead to integer solutions as soon as possible, the branching rule is used to select the next discrete variable to be branched (see Equation 6.5).

$$q = \arg\left\{ \min\left[ \min_{i \in M_N}\left( \sum_j \alpha_i^j \right), \min_{i \in M_N}\left( \sum_j \beta_i^j \right) \right] \right\} \tag{6.5}$$

where:

$$\alpha_i^j = \begin{cases} 1 \text{ if } i \in B_{Nj} \\ 0 \text{ if } i \in \overline{B}_{Nj} \end{cases} \qquad \beta_i^j = 1 - \alpha_i^j$$

$y_q$ = next variable to be branched

$\overline{B}, B$ = index sets of Boolean variables

$N$ = node that is under examination

$M$ = subset of 0-1 variables that are treated as continuous

based on the list of feasible alternatives constructed using the logic representation of the superstructure (Raman and Grossmann 1992) (see Equation 6.6).

$$\Omega_D \equiv \bigvee_{j=1}^{r}\left[ \bigwedge_{i \in B_{Nj}} \left(Y_i\right) \bigwedge_{i \in \overline{B}_{Nj}} \left(\neg Y_i\right) \right] \tag{6.6}$$

where:

$Y_i$ = existance of unit $i$

$\neg Y_i$ = non existance of unit $i$

$\Omega_D$ = list of feasible alternatives

The logical chaining approach attempts to fix as many of the other binary variables as possible by analyzing the logic representation of the superstructure (see Equation 6.7).

$$\begin{aligned} Y_i &= FALSE, \quad i \in S_0^{N+1} \\ Y_i &= TRUE, \quad i \in S_1^{N+1} \end{aligned} \tag{6.7}$$

where:

$$S_1^{N+1} = \left\{ \bigcap_{j=1}^{r} B_{N+1j} \middle| B_{N+1j} \neq \varnothing \right\}$$

$$S_0^{N+1} = \left\{ \bigcap_{j=1}^{r} \overline{B}_{N+1j} \middle| \overline{B}_{N+1j} \neq \varnothing \right\}$$

Once the variable to be branched has been selected, two new problems are created (see Equation 6.8 and Figure 6.3)

$$P_{i+1}^{i} \text{ and } P_{i+2}^{i} \tag{6.8}$$

The constraints corresponding to the selected variable and to the possible variables to be fixed are added to the problem (see Equation 6.9)

$$\begin{aligned} & y_j \geq 1 \\ & y_j \leq 0 \\ & y_{R_j} \geq 1 \\ & y_{S_j} \leq 0 \end{aligned} \tag{6.9}$$

Finally, the new problems are added to the list of open nodes, and the parent problem is deleted from the list of open nodes (see Equation 6.10)

$$P = (P \,/\, P_i^k) \cup P_{i+1}^{i} \cup P_{i+2}^{i} \tag{6.10}$$

Step 4: If at the end of the list of open nodes, there are two problems with the same parent problem do step (a); otherwise do step (b). For both cases the problems are solved using the ASPEN PLUS™ optimization block.

(a) Solve the problem $P_{i+2}^{i}$. This solution provides a value for the objective function. If this value is greater or equal than the upper bound, then this problem is eliminated from the list of open nodes. If the solution to the problem is integer go to step 6.

Solve the problem $P_{i+1}^{i}$. This solution provides a value for the objective function. If this value is greater or equal than the upper bound, then this problem is eliminated from the list of open nodes. If the solution to the problem is integer go to step 6.

If the solution to the problem *i+2* is greater or equal than the solution of the problem *i+1*, then invert the order of the problems in the list of open nodes.

(b) Solve the problem $P_i^k$. This solution provides a value for the objective function. If this value is greater or equal than the upper bound, then this problem is eliminated from the list of open nodes. If the solution to the problem is integer go to step 6.

Step 5: If the list of open nodes is empty go to step 8, otherwise go to step 3.

Step 6: If the solution is less than the upper bound, then the NLP solution becomes the new upper bound.

Step 7: Delete all nodes from the list of open nodes, for which their objective function value is greater or equal than the upper bound. Return to step 4.

Step 8: The current upper bound corresponds to the optimal solution for the MINLP problem.

A summary of the MINLP algorithm for ASPEN PLUS™ is presented in Figure 6.4 and Table 6.1. A detailed application of the algorithm for the analysis of the alternatives identified for the thermal chlorination of methane is presented in Appendix A.

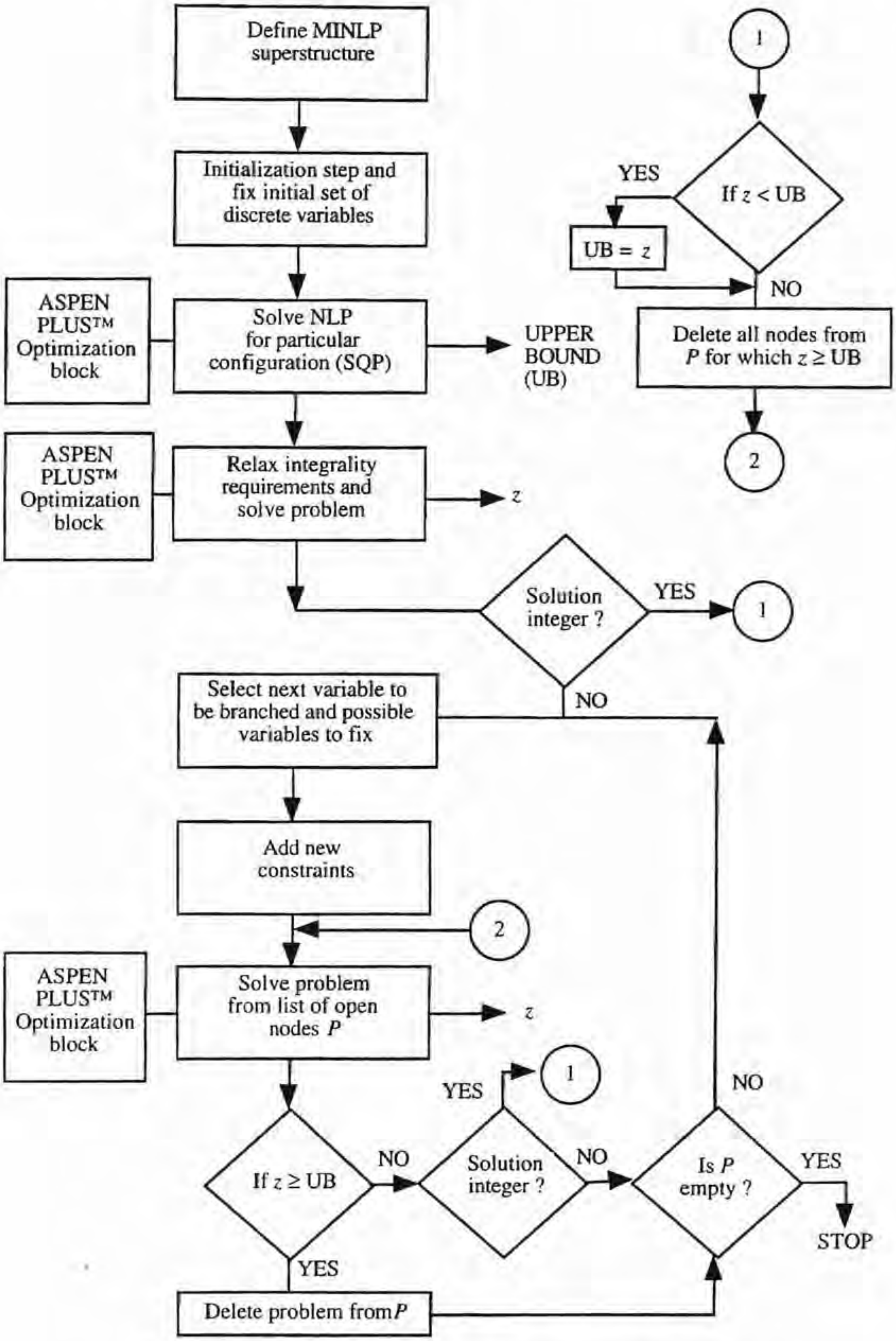

Figure 6.4: ASPEN PLUS™ MINLP Algorithm

Table 6.1: MINLP Algorithm for ASPEN PLUS™

```
Step 0: Set upper bound        $Z^u = \infty$
        List of open nodes     $P = \varnothing$
        Set initial value for  $y^1$
Step 1: Solve the initial NLP subproblem for $y^1$ $\Rightarrow$ upperbound $Z^u$
        Note: If this NLP subproblem is infeasible $Z^u = \infty$
Step 2: Relax integrality conditions of $y$
        Solve problem $P_1^0 \Rightarrow$ lower bound
        Store the problem $P = P \cup P_1^0$
        If solution is integer $\Rightarrow$ step 6
Step 3: Take last problem $P_i^k$
        Calculate $q$ and pick a binary value $y_j$
        Determine possible variables to be fixed $\Rightarrow S_0^{i+1}, S_1^{i+1}, S_0^{i+2}, S_1^{i+2}$
        Create two new problems $P_{i+1}^i$ and $P_{i+2}^i$
        Add constraints $\left(y_j \ge 1 \vee y_j \le 0\right) \wedge \left(y_{R_j} \ge 1\right) \wedge \left(y_{S_j} \le 0\right)$
        $P = \left(P / P_i^k\right) \cup P_{i+1}^i \cup P_{i+2}^i$
Step 4: If at end of the list there are two problems with the same parent problem
        do step (a); otherwise do step (b)
        (a) Solve $P_{i+2}^i \Rightarrow z_{i+2}^i$        If $z_{i+2}^i \ge Z^u \Rightarrow P = P \setminus P_{i+2}^i$
                                          If solution is integer $\Rightarrow$ step 6
            Solve $P_{i+1}^i \Rightarrow z_{i+1}^i$        If $z_{i+i}^i \ge Z^u \Rightarrow P = P \setminus P_{i+1}^i$
                                          If solution is integer $\Rightarrow$ step 6
            If $z_{i+2}^i \ge z_{i+i}^i \Rightarrow$ invert $P_{i+1}^i$ and $P_{i+2}^i$
        (b) Solve $P_i^k$                 If $z_i^k \ge Z^u \Rightarrow P = P \setminus P_i^k$
                                          If solution is integer $\Rightarrow$ step 6
Step 5: If $P = \varnothing \Rightarrow$ step 8; otherwise $\Rightarrow$ step 3
Step 6: Solve NLP subproblem fixing the binary variables obtained $\Rightarrow Z_{NLP}$
        If $Z_{NLP} < Z^u \Rightarrow Z^u = Z_{NLP}$
Step 7: Delete nodes $P_i^k$ from the list $P$ for which $z_i^k \ge Z^u$
        Return to step 4
Step 8: The current upper bound $Z^u$ is the optimal solution to the MINLP
```

## Process Integration

The process integration tool was originally developed during the energy crisis in the 1980's. The main purpose is to maximize the heat transfer between the process streams and minimize the requirements of external utilities. Thus, by recovering the energy generated in a process, the utility requirements are satisfied and the utility cost is minimized. The retrofit of heat exchanger networks (HEN) has been accomplished by formulating the problem as an MINLP problem. Two general approaches have been suggested. These are the one-to-one approach (Ciric and Floudas 1990) and the one-to-many approach (Yee, et al. 1990). These two approaches have been successfully applied to retrofit HEN networks and include all possible network configurations. The constraints on heat loads and stream matches are more easily introduced in the one-to-one approach (Papalexandri and Pistikopoulos 1993). There is no reference in the literature regarding the identification of optimum HEN configurations using ASPEN PLUS™. Both approaches were evaluated using ASPEN PLUS™, and the one-to-one approach was easier to represent using this process simulator.

The one-to-one approach consists of the representation of all of the possible HEN configurations through the use of a superstructure. The input to the superstructure corresponds to a set of cold streams *I* and a set of hot streams *J*. A cold stream is defined as a process stream that is to be heated, and a hot stream is defined as a process stream that is to be cooled. Each potential match in the superstructure, corresponds to the existence of a heat exchanger unit which may be present or purchased. The bypass of a specific heat exchanger unit is also considered through the use of splitters and mixer blocks. The proposed methodology will assume that the utilities supply the necessary heat duty for the required heat load. The heat duty supplied by the utilities will correspond to the heat load that could not be supplied internally by the process streams. This is accomplished by adding the utility matches at the end of the superstructure (see Figure 6.5), where

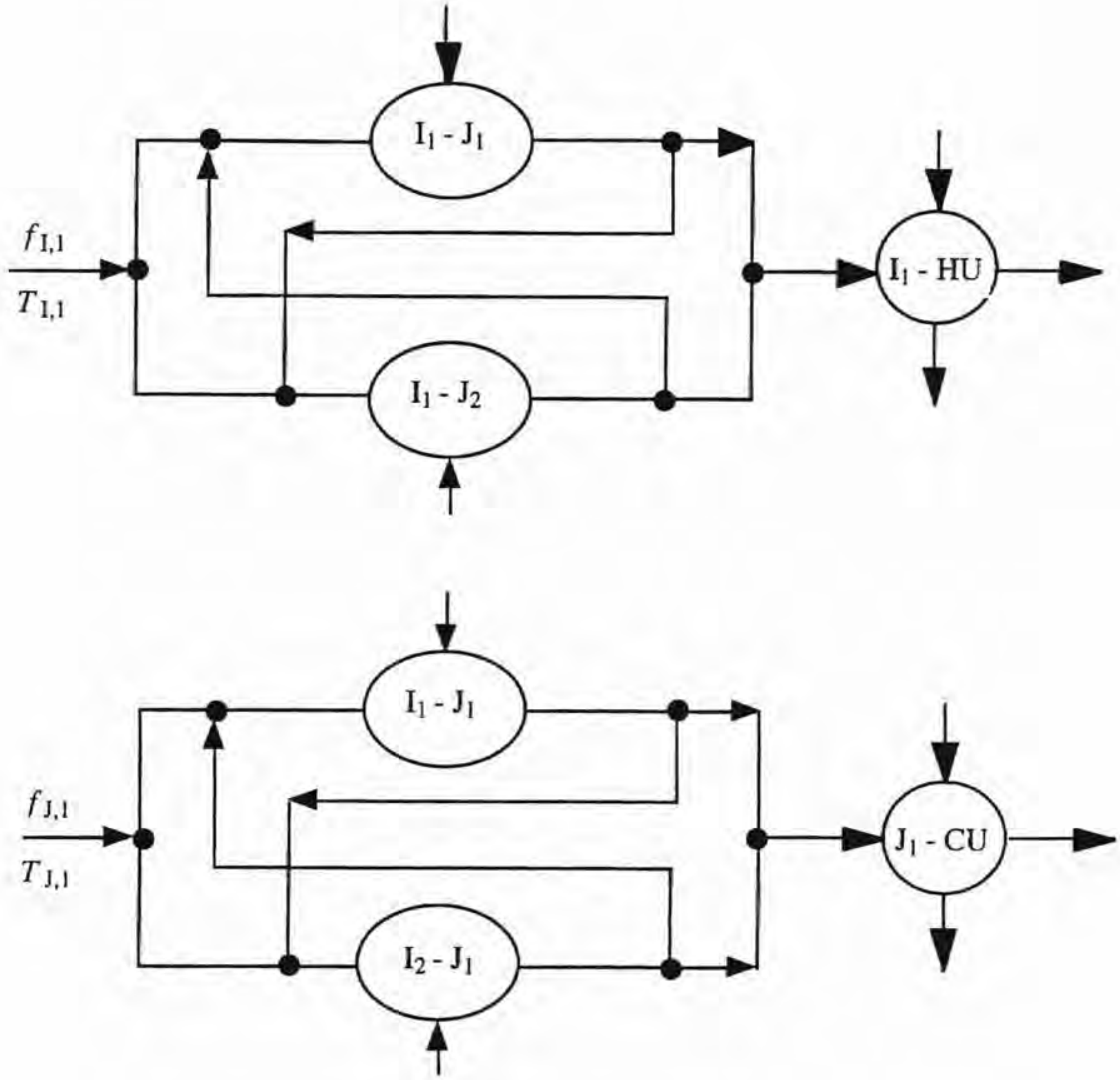

Figure 6.5: HEN Superstructure

$f$ = Flowrate

T = Temperature

HU = Hot utility

CU = Cold utility

$I_1$ = Cold stream 1

$I_2$ = Cold stream 2

$J_1$ = Hot stream 1

$J_2$ = Hot stream 2

$I_1$ - $J_1$ = Heat exchanger between streams $I_1$ and $J_1$

$I_1$ - $J_2$ = Heat exchanger between streams $I_1$ and $J_2$

$I_2$ - $J_1$ = Heat exchanger between streams $I_2$ and $J_1$

$I_1$ - HU = Heat exchanger between stream $I_1$ and HU

$J_1$ - CU = Heat exchanger between stream $J_1$ and CU

The following assumptions are made: (1) the heat exchangers are of the countercurrent type, (2) only one match between two streams is allowed, and (4) no matches between hot streams or between cold streams is allowed.

The use of ASPEN PLUS™ for the formulation of the HEN superstructure, presents several advantages due to the existing internal constraints such as mass and energy balances that are not required to be specified as part of the optimization block. Each potential heat exchanger unit is represented in ASPEN PLUS™ with a HEATER block, and the mixer and splitter units with FSPLIT and MIXER blocks respectively.

The minimum temperature difference $\Delta T_{min}$ between streams that are to exchange heat, represents a critical parameter in a process integration study. The $\Delta T_{min}$ used will have an effect on the utilities and capital costs (see Figure 6.6).

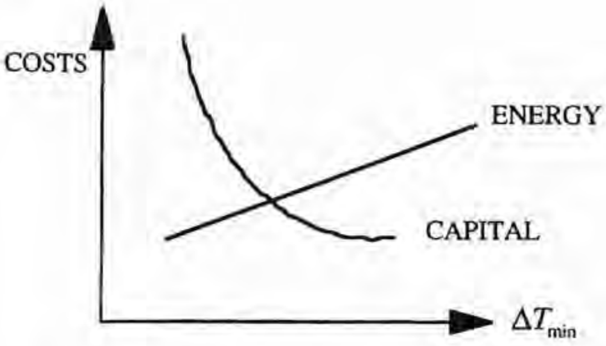

Figure 6.4: $\Delta T_{min}$ cost effect (Linnhoff, et al. 1982)

The value of $\Delta T_{min}$ can vary between 18 and 72 °F, and there is no straight forward method to locate this point accurately (Linnhoff, et al. 1982). A recommended value for $\Delta T_{min}$ has been suggested to be 18 °F (10 K). Polley (1993) presents the physical implications for the use of $\Delta T_{min}$, and suggests minimum values to be applied to correctly design heat exchangers. These values depend on the type of unit to be used and their classification (single-phase exchangers, vaporizers and reboilers, and condensers). For the case of single-phase heat exchangers a minimum value of 18 °F is required. A minimum value of 45 °F is required for vaporizers, reboilers, and condensers. For the present study the $\Delta T_{min}$ was taken as 18 °F.

## Economic model for process integration

An evaluation of a heat exchanger network modification needs to consider not only the utility costs and capital costs associated with heat exchanger area, but also the cost of reassigning existing units at different matches and the cost of repiping streams. The cost of repiping streams can vary between 4-20% of the capital costs (Peters and Timmerhaus 1991). To accurately estimate this effect, layout considerations should be included in the economic model (Adriani, et al. 1995). The capital cost $CF$ for each potential match was calculated using Equation 6.11 (Douglas 1988).

$$CF = \frac{M\&S}{280}\left(101.3\left(\frac{Q}{U(LMTD)}\right)^{0.65} F_c\right) \qquad (6.11)$$

where

$M\&S$ = Marshall & Swift Index

$Q$ = Heat exchanger load (Btu/hr)

$U$ = Overall heat transfer coefficient (Btu/ft$^2$ hr °F)

$LMTD$ = Logarithmic mean temperature difference (°F)

$F_c$ =( $F_d$+ $F_p$) $F_m$

$F_m$ = Design material factor

$F_p$ = Design pressures factor

$F_d$ = Design type factor

The design factor $F_c$ was taken as 1, assuming a carbon steel floating head heat exchanger and a design pressure of up to 150 psi. Perry and Green (1984) present values for the overall heat transfer coefficient $U$ that can be used for preliminary estimating purposes. The overall heat transfer coefficient was assumed as 149.67 Btu/ft$^2$ hr °F (Aspen Technology 1988). Finally, an approximation for the logarithmic mean temperature difference (LMTD) is used to avoid numerical difficulties when the approach temperatures of both sides of the exchanger are equal (Yee, et al. 1990) (see Equation 6.12)

$$LMTD \approx \left[(\Delta t_1)(\Delta t_2)\frac{\Delta t_1 + \Delta t_2}{2}\right]^{1/3} \qquad (6.12)$$

where:

$\Delta t_1$ = temperature difference at hot end of heat exchanger

$\Delta t_2$ = temperature difference at cold end of heat exchanger

The MINLP problem for retrofitting heat exchanger networks using ASPEN PLUS™ consists of the representation of the HEN using a superstructure (see Figure 6.2) and an objective function (see Equation 4.4). The continuous variables $x$ will be represented by varying the heat flow to each possible match, through the use of heat streams. Each possible match is represented by two HEATER blocks, therefore, additional constraints are added to consider both blocks as one unit (see Equation 6.13).

$$Q_{I,J} + Q_{J,I} = 0 \qquad \text{for } I = 1 \ldots \mathrm{I} \;\text{ and } J = 1 \ldots \mathrm{J} \tag{6.13}$$

Since all the physical constraints are already specified by ASPEN PLUS™, the only added constraint will be to specify the value for $\Delta T_{min}$ (see Equation 6.14 and 6.15).

$$\Delta T_{J,I} \geq \Delta T_{\min} \qquad \text{for } I = 1 \ldots \mathrm{I} \;\text{ and } J = 1 \ldots \mathrm{J} \tag{6.14}$$

$$\Delta T_{I,J} \geq \Delta T_{\min} \qquad \text{for } I = 1 \ldots \mathrm{I} \;\text{ and } J = 1 \ldots \mathrm{J} \tag{6.15}$$

Additional constraints may be added to specify specific temperatures and to specify that stream splitting is not allowed. As with the case of the flowsheet superstructure, an initial guess for the heat flow of each stream is required. The starting point can be estimated by calculating the maximum heat load required by a specific stream.

The optimal flowsheet defined is used to construct the HEN superstructure and to evaluate the best heat exchanger network configuration. The superstructure is constructed using the one-to-one approach. The correct angle to the process integration should be to consider both the flowsheet and HEN optimization simultaneously. Due to the size of the problem, the optimization was done in a sequential analysis. This method does not explicitly consider the capital costs for heat exchangers during the superstructure analysis, but a good estimate can be assumed since this costs are a function of the utility requirements of each process alternative. For this method additional constraints are added to specify the required outlet temperatures of each stream, have to be met by varying the heat flow to each heat exchanger.

This chapter presented the development of the superstructure containing all the previously defined process retrofit alternatives. This superstructure is formulated as an MINLP problem and solved with a modified LP/NLP based branch and bound algorithm, that includes the DNF approach to reduce the number of nodes to evaluate. The solution of the MINLP problem gives an optimum flowsheet configuration. This configuration is further analyzed by selecting the optimum HEN configuration using the one-to-one approach, to minimize the energy requirements of the process.

In summary the proposed methodology (see Figure 3.1) consists of four general steps:

A. Development of base case model (see Chapter V)
   1. Gathering of process information (see Table 3.1)
   2. Construction of base case model using ASPEN PLUS™ process simulator
   3. Development of economic model (see Chapter IV)

B. Generation of process retrofit alternatives (see Chapter V)
   1. Zero investment level
   2. Variable investment level
      a. Input information
      b. Input - output structure of flowsheet
      c. Recycle structure
      d. Separation system

C. Evaluation and optimization of process alternatives (see Chapter VI)
   1. Formulation of superstructure
   2. Inclusion of logic constraints
   3. Solution of MINLP problem
   4. Formulation of HEN superstructure
   5. Solution of HEN superstructure

D. Evaluation of future scenarios

The next chapter presents the application of the proposed methodology to a specific process. The process selected was the production of methyl chloride through the thermal chlorination of methane.

# CHAPTER VII

# CASE STUDY

This chapter presents the application of the proposed methodology to a specific process: the production of methyl chloride by the thermal chlorination of methane. This process was selected because of the environmental impact and potential for improvement. There is not a reported study in the literature where a simulation of the complete process, an economic analysis, or a waste reduction study has been done. The chapter is divided in four general sections: (1) process description, (2) base case process model, (3) generation of process retrofit alternatives, and (4) evaluation of process retrofit alternatives.

## PROCESS DESCRIPTION

(Part A.1 of methodology)

Methyl chloride ($CH_3Cl$ ), also known as chloromethane, was first prepared in 1835 by Dumas and Peligot. Methyl chloride is a colorless gas with a mild odor and a sweet taste (Holbrook 1993). It is handled commercially as a liquid. Most of the methyl chloride produced (79%) is used for the manufacture of silicones, particularly, as the starting point in the Rochow synthesis (Morreto, et al. 1985). Other uses include the manufacture of methyl cellulose, agricultural chemicals, quaternary amines and butyl rubber (Chemical Profiles 1992). The methyl chloride U.S. demand (Chemical Profiles 1992) was 785 and 794 million pounds for 1991 and 1992 respectively, and is estimated to be 845 million pounds by 1996.

## Process Chemistry

The feed to the reactor is a mixture of chlorine and methane which react to give methyl chloride. Subsequent reactions give methylene chloride ($CH_2Cl_2$ ), chloroform ($CHCl_3$ ) and carbon tetrachloride ($CCl_4$ ), as well as substantial amounts of hydrogen chloride (HCl) (See Scheme I).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl \qquad \text{Scheme I}$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

The feed to the reactor must be heated to 572 °F for the reaction to be initiated. It has been found in commercial operations that an operating temperature of 752 to 842 °F is necessary to have a stable, self sustaining reaction. The reactor should not be operated higher than 932 °F since pyrolysis can occur, being a very exothermic reaction, that can lead to a possible reactor explosion. The reactor should also not be operated at high pressures to prevent any risks that could lead to a safety hazard.

The methane feed should contain a minimal amount of impurities ( $1\times10^{-4}$ $ft^3$ / $ft^3$ of solution, excluding $N_2$) (DeForest 1979). Under certain conditions (Johnson, et al. 1959) such as high impurities and both low and high mole feed ratios, the process can yield vinyl chloride, vinylidene chloride, 1,2-dichloroethylene, ethylidene dichloride, methyl chloroform, ethylene dichloride, and trichloroethylene. Apart from the regulation status of these by-products, they can generate subsequent problems during the separation sequence.

## Process

The methyl chloride process consists primarily of a CSTR where the four reactions take place. The reactor effluent is cooled to 77 °F and is washed with water to remove the hydrogen chloride (HCl) generated. The water stream becomes a waste that contains both

HCl and a small amounts of chloromethanes. The chloromethanes mixture is then dried to remove the water. This is accomplished through a series of dehumidification towers containing sodium hydroxide (NaOH) and sulfuric acid ($H_2SO_4$), generating several waste streams. The water content in the process streams should be less than $5x10^{-5}$ $ft^3$ / $ft^3$ of solution to minimize corrosion and to prevent hydrolysis and decomposition of the chloromethanes. As the next step, part of the mixture is recycled back to the reactor. The mixture is then compressed and passed through a series of distillation columns to separate each of the four products (Student Contest Problem 1964) (see Figure 7.1).

## Regulations

Methyl chloride and the corresponding by-products methylene chloride ($CH_2Cl_2$), chloroform ($CHCl_3$), and carbon tetrachloride ($CCl_4$) are considered hazardous wastes under RCRA and are regulated by the CWA, CAA, and included in the HON. Methylene chloride, a suspected carcinogen, chloroform, and carbon tetrachloride are also included in the 33/50 program (Freeman, et al. 1992). Fugitive emissions of carbon tetrachloride need to be eliminated by the year 2000 according to the Montreal Protocol, and a ban on its production goes in effect by 1996. The by-products identified by Johnson, et al. (1959) are also regulated under RCRA, CWA, CAA, and HON. Methyl chloroform and trichloroethylene are also included in the 33/50 program. A summary of these regulations is presented in Table 7.1.

The process generates several waste streams. An attempt will be made to minimize or eliminate these waste streams:

1. Stream leaving the absorber containing HCl, water, and chloromethanes.
2. Waste streams leaving the drying towers.
3. The amount of by-products generated.
4. Heavy ends after the distillation sequence.

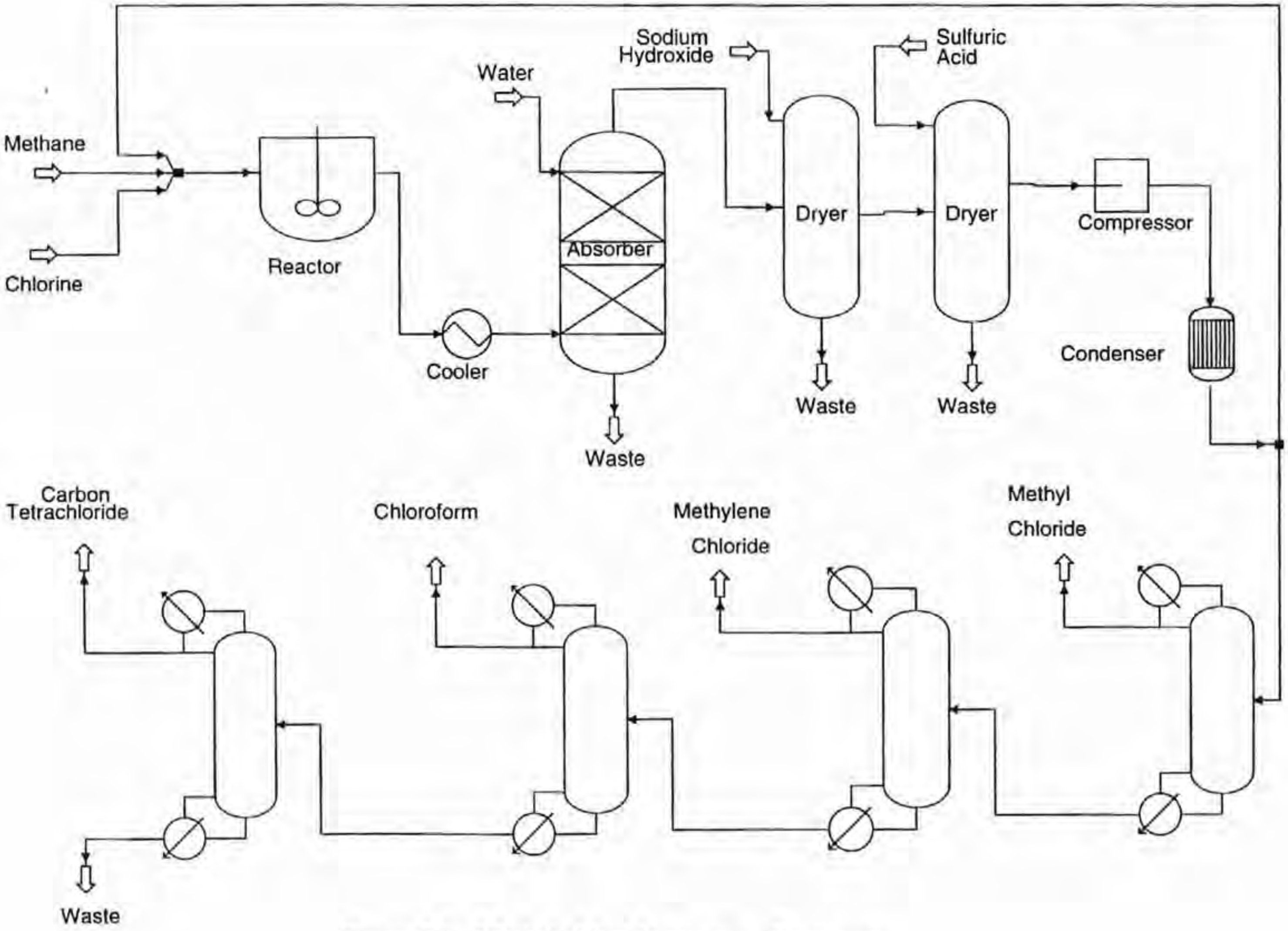

Figure 7.1: Methyl chloride process - Base case

Table 7.1: Summary of regulations for methyl chloride process

| Regulation | Methyl Chloride | Methylene Chloride | Chloroform | Carbon Tetrachloride | Other ** |
|---|---|---|---|---|---|
| RCRA | X | X | X | X | X |
| CWA | X | X | X | X | X |
| CAA | X | X | X | X | X |
| HON | X | X | X | X | X |
| 33/50 |  | X | X | X | X |
| Priority Poll. | X | X | X | X | X |
| Carcinogen |  | X |  |  |  |
| Production ban |  |  |  | X |  |

** Includes: Methyl chloroform and trichloroethylene

## BASE CASE PROCESS MODEL

This section presents the development of the base case model (Part A.2 of methodology). The process used for this study is the production of methyl chloride by the thermal chlorination of methane. The base case reported (Student Contest Problem 1964) was taken as the current process in operation. The reported variables for the process used to model the base case situation are shown in Table 7.2. The values used to model the base case were taken as quoted, except for the reaction temperature that is not to exceed 932 °F because pyrolysis may occur. For the base case model, a reaction temperature of 842 °F was assumed.

### Synthesis Step

The synthesis step consists of a continuously stirred tank reactor (CSTR) where the four reactions take place (see Scheme I). The ASPEN PLUS™ block RCSTR was used to model the reactor. This block uses the power law expression to define the reaction kinetics (see Equation 7.1).

Table 7.2: Reported Input Variables

| Variable | Value |
|---|---|
| Feed ratio ($Cl_2$ / $CH_4$) | 0.3 |
| Reactor type | Isothermal CSTR |
| Reaction temperature | 977 °F |
| Reactor effluent cooling system | 77 °F |
| Condenser temperature | -58 °F |
| Compressor outlet pressure | 115 lb/in$^2$ |
| Product demand | 160 lbmol/hr |

Source: Student Contest Problem (1964)

$$r = AT^{a}e^{-E_a/RT}\prod(C_i)^{b_i} \tag{7.1}$$

The reported kinetic data (Scipioni and Rapisardi 1961) was available in pressure units. To convert to the required units, the data was extracted from the available source, recalculated and replotted (Smith 1981). The final values are shown in Table 7.3.

Table 7.3: Kinetic parameters for base case model (Scheme I)

| Reaction Number | Rate Equation | Pre-exponential factor $\left[\sec\cdot\frac{\text{lbmol}}{\text{ft}^3}\right]^{-1}$ | Activation energy $\frac{\text{Btu}}{\text{lbmol}}$ |
|---|---|---|---|
| 1 | $k_1[Cl_2][CH_4]$ | 4.10 x $10^9$ | 35260 |
| 2 | $k_2[Cl_2][CH_3Cl]$ | 1.01 x $10^9$ | 30580 |
| 3 | $k_3[Cl_2][CH_2Cl_2]$ | 4.10 x $10^9$ | 35260 |
| 4 | $k_4[Cl_2][CHCl_3]$ | 4.69 x $10^9$ | 37490 |

Note: The Pre-exponential factor needs to be in SI units to be included in ASPEN PLUS™

Source: Scipioni, 1961

The product distribution will vary with temperature and molar feed ratio. Several sources exist in the literature that predict the product composition based on the feed ratio (DeForest 1979; Johnson, et al. 1959; McBee, et al. 1942; Scipioni and Rapisardi 1961). The RCSTR block of ASPEN PLUS™ was used to determine the validity of the model by performing a product distribution study as a function of feed ratio (see Figure 7.2). The behavior obtained in Figure 7.2 corresponds to reported behaviour in the literature. As expected the methyl chloride produced decreases as the molar feed ratio increases, whereas an increase in carbon tetrachloride is obtained as the molar feed ratio increases. By analyzing the results presented in Figure 7.2, a low feed ratio will maximize the production of methyl chloride and minimize the production of byproducts.

The feed to the reactor needs to be of high purity. DeForest (1979) suggests that the methane feed should not contain more than $1 \times 10^{-4}$ $ft^3$ / ($ft^3$ of solution) of impurities excluding nitrogen, to prevent the chlorination of other hydrocarbons present. The methane used in the process is usually obtained from natural gas, which can be an important source for impurities (see Table 7.4). The methane is purified to remove other hydrocarbons through cryogenic distillation.

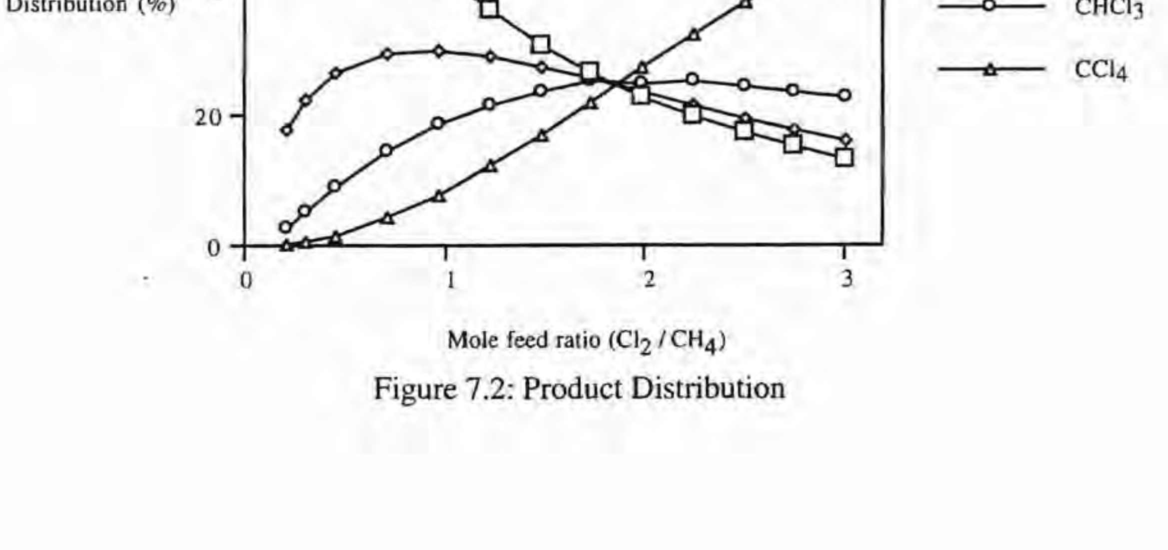

Figure 7.2: Product Distribution

Table 7.4: Natural gas composition

| Component | Average composition<br>% Volume |
|---|---|
| Methane | 89.90 |
| Ethane | 5.10 |
| Propane | 1.54 |
| Butanes | 0.36 |
| Pentanes | 0.097 |
| Hexanes plus | 0.038 |
| $CO_2$ | 0.565 |
| $N_2$ | 2.39 |

Source: Perry and Green (1984)

### Separation Step

The reactor effluent is cooled to the specified temperature of 77 °F, and is then passed through an absorber where the HCl is removed by using water as the absorbing agent. To adequately represent this operating unit the dissociation of HCl in water has to be taken into account. Among the different data banks and chemistries available in ASPEN PLUS™, Equation 7.2 (data bank H2OHCL)

$$HCl \leftrightarrow H^+ + Cl^- \qquad (7.2)$$

gives the best results when compared to experimental data (Oldershaw, et al. 1947). The data package H2OHCL uses the electrolyte NRTL and Henry's Law models. The latter requires Henry's Law constants for interactions between water and the different components. Although ASPEN PLUS™ has several data sources for interaction parameters, ASPEN PLUS™ does not include information for the interactions between $H_2O$ - $CH_2Cl_2$, $H_2O$ - $CHCl_3$, and $H_2O$ - $CCl_4$. The reported values for these interactions (Gossett 1987) were correlated as a function of temperature *T* in the form of Equation 7.3. The final values in are shown in Table 7.5.

$$H=exp(H_1-H_2/T) \tag{7.3}$$

Table 7.5: Henry's Law Constants

| Component | $H_1$<br>$\frac{ft^3\ psi}{lbmol}$ | $H_2$<br>$\frac{ft^3\ psi\ °R}{lbmol}$ | Temperature Range<br>°F |
|---|---|---|---|
| $CH_2Cl_2$ | 13.65 | 6871 | 50 - 95 |
| $CHCl_3$ | 16.84 | 8302 | 50 - 95 |
| $CCl_4$ | 18.28 | 7940 | 50 - 95 |

Note: The tabulated values need to be in SI units to be included in ASPEN PLUS™

Source: (Gossett 1987)

The next step in the separation sequence is the removal of the water introduced in the previous step. The concentration of water throughout the process is recommended to be less than $5x10^{-5}$ $ft^3$ / $ft^3$ of solution (DeForest 1979). This minimizes corrosion when the streams contain HCl or chlorine and prevents the hydrolysis and decomposition of the product and by-products in subsequent steps. The removal of water is usually accomplished with a series of drying columns by using sulfuric acid and sodium hydroxide as drying agents. There is not much information available regarding this process, and since one of the proposed alternatives is the removal of water, the elimination of this step will be considered. This step will be represented with an ASPEN PLUS™ SEP block. The economic criteria used to evaluate the performance of this unit is based in the amount of waste generated, which is a function of the amount of water to be removed.

The final step in the separation sequence is a series of distillation columns where the product and each of the by-products are separated. The ASPEN PLUS™ DSTWU shortcut distillation method was used to obtain an initial estimate of the basic parameters. The DSTWU block uses Winn's method to estimate the minimum number of stages, Underwood's method to estimate the minimum reflux ratio, and Gilliland's correlation to estimate the required reflux ratio or the required number of stages (Schweitzer 1988). The values obtained from applying the DSTWU block were incorporated into a more rigorous separation model RADFRAC.

A summary of the blocks used to represent the different operating units is shown in Table 7.6. The input file corresponding to the base case is presented in Appendix B and the ASPEN PLUS™ block diagram for the base case is presented in Figure 7.3.

Table 7.6: Summary of base case blocks

| Operating Unit | Block used |
|---|---|
| Reactor | RCSTR |
| Cooling system | HEATER |
| Absorber | RADFRAC |
| Dryer | SEP |
| Condenser | HEATER |
| Compressor | COMPR |
| Distillation Columns | RADFRAC |

The absorber model used for the base case process is computationally intensive. Several case studies were done using the absorber model. Based on the absorber model, a relationship was made to determine the amount of water required as a function of the amount of hydrogen chloride (see Equation 7.4 and Figure 7.4).

$$f_{H_2O} = 4.855 f_{HCl} - 6.143 \tag{7.4}$$

where:

$f_{H_2O}$ = molar flowrate of water used as the absorbing agent

$f_{HCl}$ = molar flowrate of HCl entering the absorber

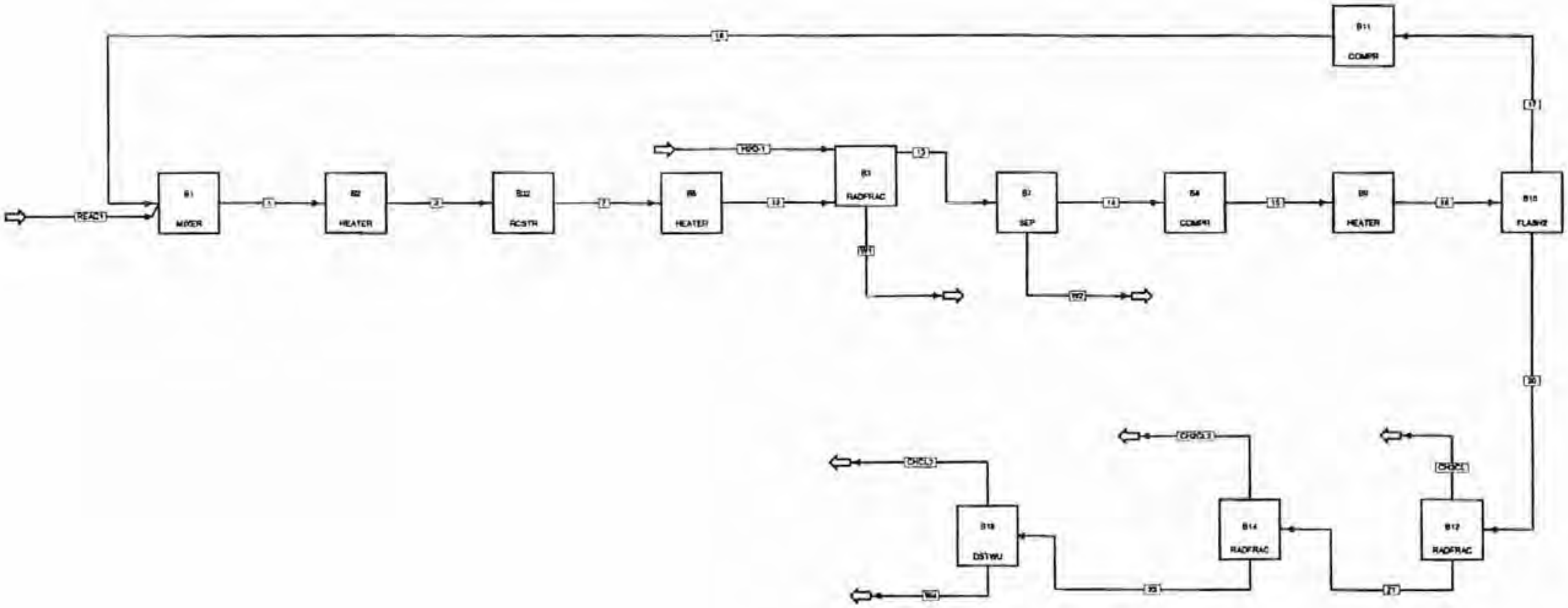

Figure 7.3: ASPEN PLUS™ block diagram for the base case process

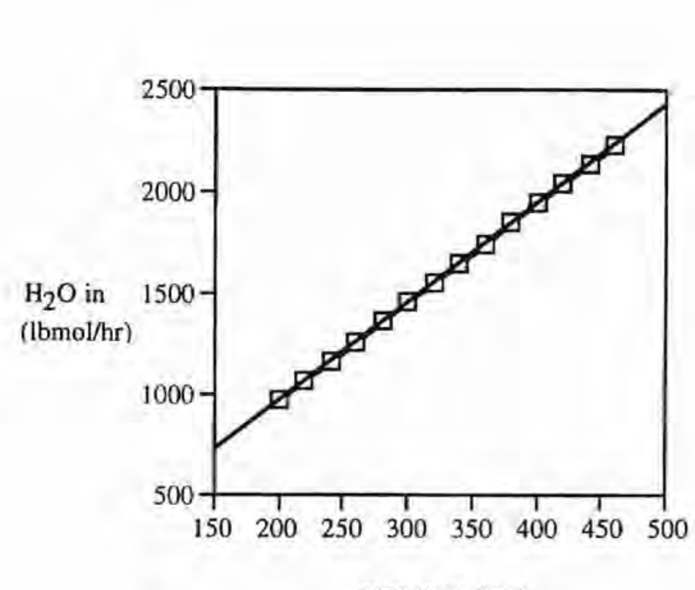

Figure 7.4: Absorber Correlation

The average recovery for hydrogen chloride and water was 99.9% and 24.9% respectively. A computational time comparison was made between using the absorber model and the calculated relationship. The base case model is evaluated in 44.6 seconds of CPU time, whereas the inclusion of the absorber requires 1082.8 seconds of CPU time. The absorber model was replaced with an ASPEN PLUS™ SEP block, and the new model was further incorporated in the superstructure.

### Economic Model for Base Case
### (Part A.3 of methodology)

The economic data for the base case model is summarized in Table 7.7. All prices quoted are for a specified project date of January 1995. For the case where the effective date of the prices quoted differed from the project date, the values were adjusted using Marshall and Swift equipment cost index (Peters and Timmerhaus 1991). The prices for raw materials were taken from the Chemical Marketing Reporter (1995). The methane feed to the process has to be of a very high purity, thus the purchase price of methane was increased to take into account its purification through cryogenics (Jordan 1972). The quoted industrial rates for water and electricity were given by the City of Stillwater. The cost of the heating utilities was taken from Douglas (1988). The refrigeration system was taken as a single stage propylene system, capable of delivering the required temperatures (Gas Processors Suppliers Association 1994). For the waste costs a value of 0.23 \$/lb was assumed, corresponding to the 2 to 1 ratio rule. The economic data is used to construct the economic model (see Equation 7.5 and 7.6).

$$Mc_B = Rw_B + W_B + O_B + Ac_B \tag{7.5}$$

$$O = \sum_{i=1}^{Y} (utility\ consumption_i)(utility\ cost)_i \tag{7.6}$$

Table 7.7: Economic data for base case process

| | |
|---|---|
| Raw materials | |
| Chlorine | 0.113 \$/lb |
| Methane (includes purification) | 0.0722 \$/lb |
| Water | $1.98 \times 10^{-4}$ \$/lb |
| Waste cost | 0.23 \$/lb |
| Utilities | |
| Cooling water | $6.59 \times 10^{-6}$ \$/Btu |
| Refrigeration | |
| Condenser system | $1.16 \times 10^{-5}$ \$/Btu |
| Compressor system | $1.50 \times 10^{-5}$ \$/Btu |
| Heating utilities | $5.96 \times 10^{-6}$ \$/Btu |
| Electricity | $2.05 \times 10^{-5}$ \$/Btu |

## SELECTION OF PROCESS RETROFIT ALTERNATIVES

This section presents the identification of feasible alternatives to be further evaluated and optimized (Part B of methodology). There are two levels of possible alternatives. The zero investment level considers the modification of existing operating parameters, thus requiring no major investments. The second level of alternatives also referred as the variable investment level considers possible flowsheet structure modifications that may require capital investment.

### Zero Investment Level

The sensitivity analysis in this level was used to evaluate each variable of the base case process (Part B.1 of methodology). The variables that showed an important effect in the overall performance of the process were identified as possible retrofit alternatives for waste minimization. The final variables identified are the reaction temperature, reactor pressure, molar feed ratio and compressor outlet pressure (see Figures 7.2, 7.5 to 7.11). The molar feed ratio graphs (see Figure 7.2, 7.5 to 7.8) are presented as a function of the product distribution, in order to compare the model to the reported behavior. The economic performance of the model is directly related to this product distribution. The reactor should be operated at low pressures to prevent any safety risks. Therefore, the pressure in the system was optimized in two points, the reactor system pressure an the compressor pressure as the starting point for the final distillation sequence.

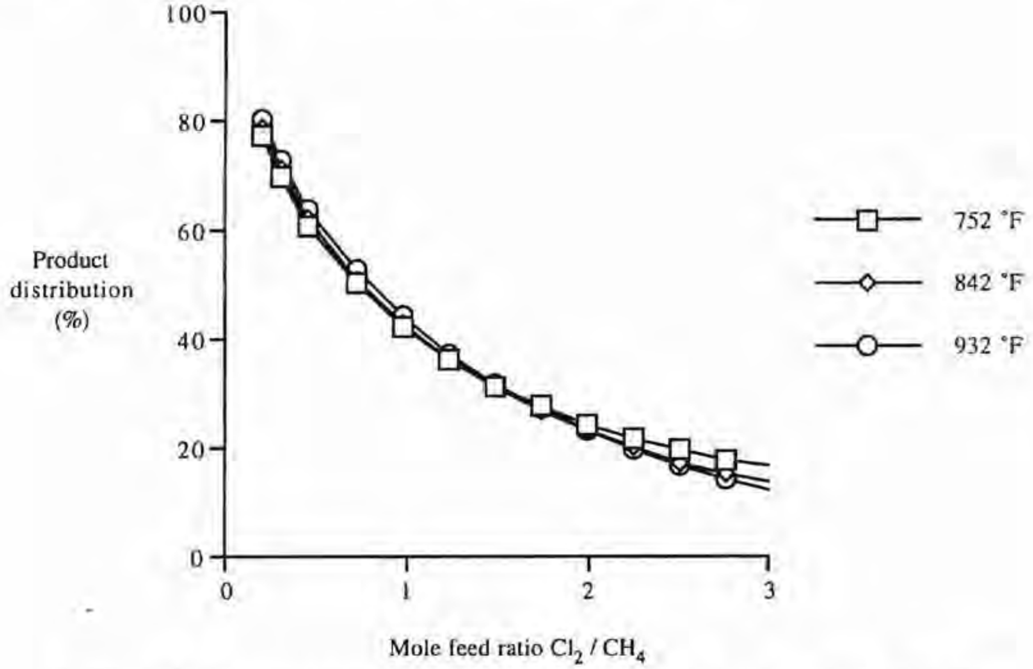

Figure 7.5: Temperature effect on methyl chloride distribution - base case

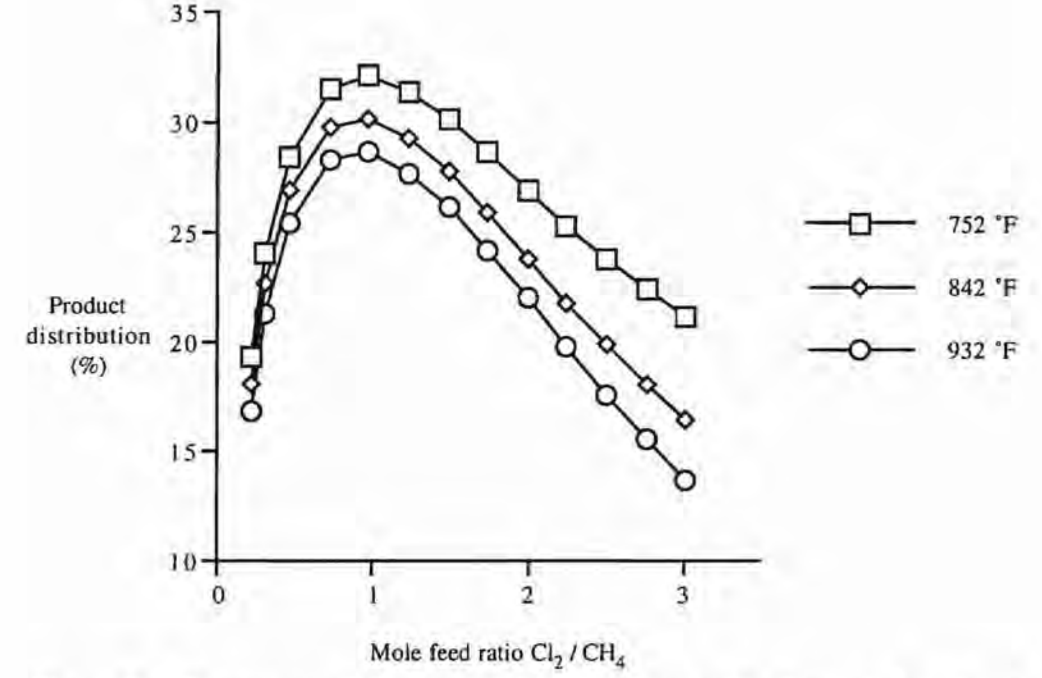

Figure 7.6: Temperature effect on methylene chloride distribution - base case

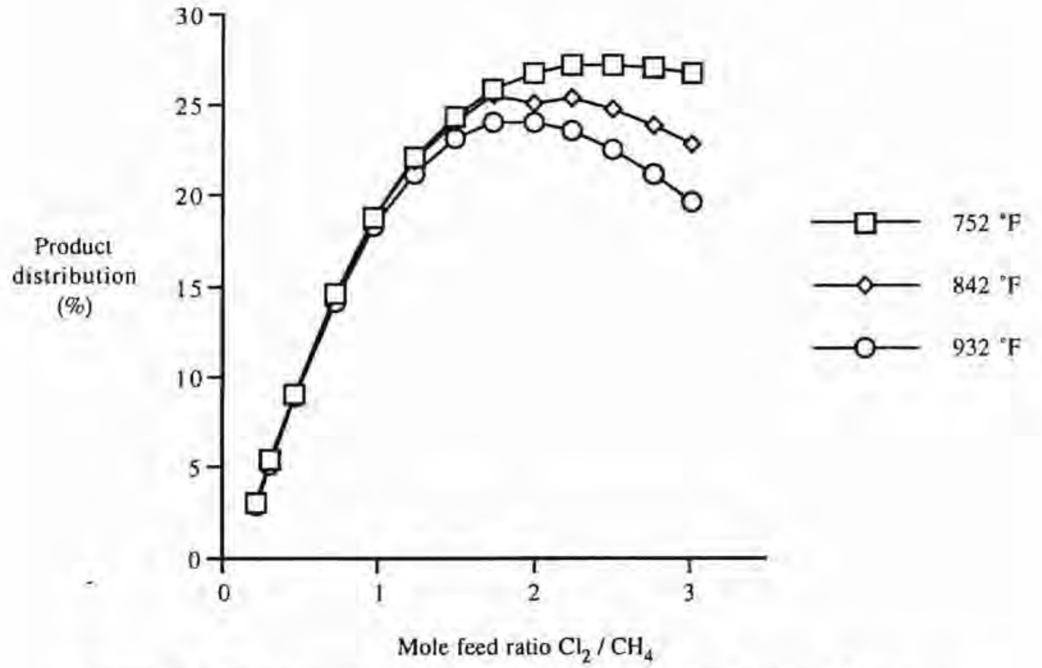

Figure 7.7: Temperature effect on chloroform distribution - base case

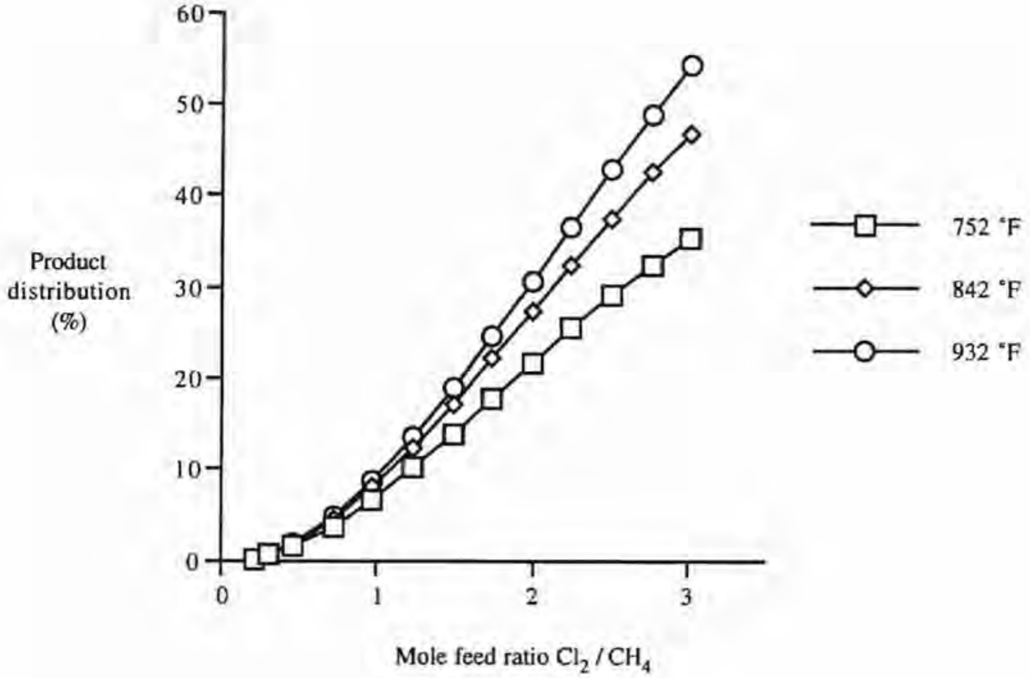

Figure 7.8: Temperature effect on carbon tetrachloride distribution - base case

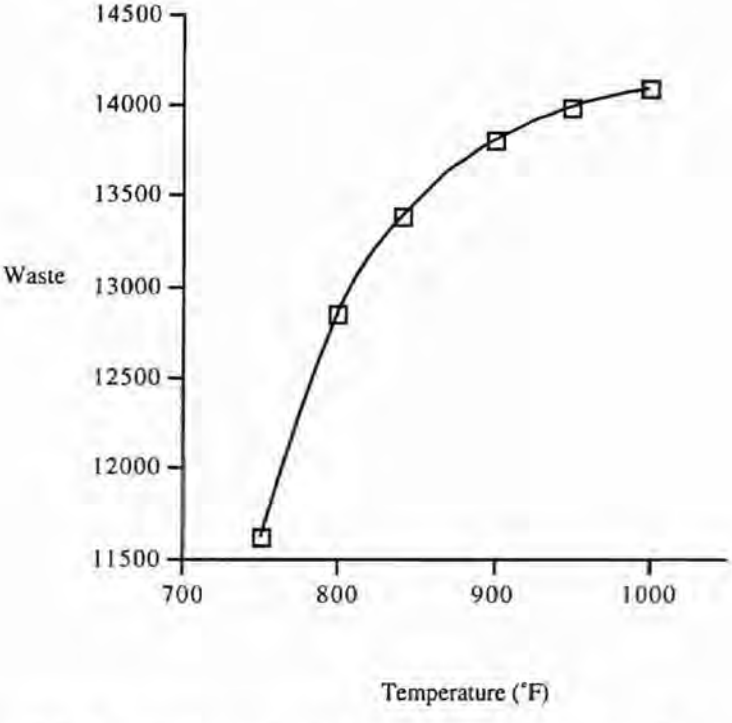

Figure 7.9: Sensitivity analysis for reactor temperature - base case

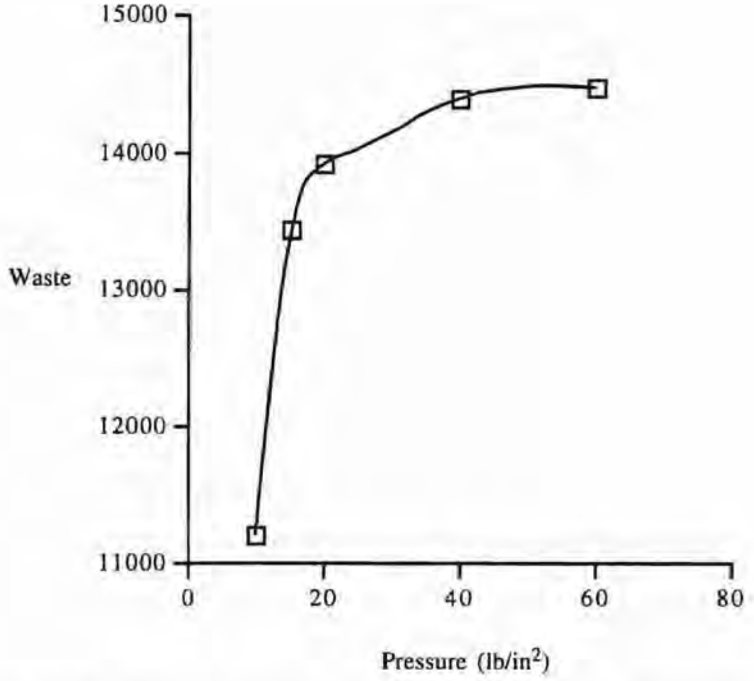

Figure 7.10: Sensitivity analysis for reactor pressure - base case

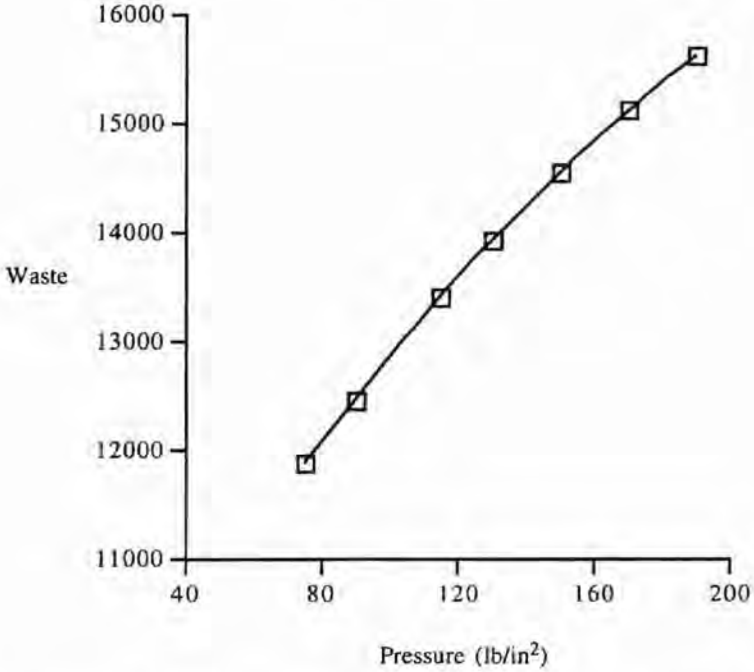

Figure 7.11 Sensitivity analysis for compressor pressure - base case

## Variable Investment Level

This level serves to identify the feasible flowsheet structure alternatives (Part B.2 of methodology). This is accomplished through the use of a hierarchical procedure (see Table 5.1).

Level 1 - Input information (Part B.2.a of methodology): The information required for this level was similar to that already present for the base case. Regarding the process chemistry, the waste minimization approach requires the evaluation of possible alternative reaction schemes that will be more environmentally friendly. Through this analysis, the use of the hydrochlorination of methanol was selected as an alternative chemistry. The same analysis applying the hierarchical procedure to the hydrochlorination of methanol is presented in the next section.

Level 2 - Input output structure of flowsheet (Part B.2.b of methodology): The methane feed to the reactor has to be free of impurities. The methane used is usually obtained from natural gas (see Table 7.4). The various hydrocarbons easily react with chlorine to form chlorinated wastes such as vinyl chloride, vinylidene chloride, 1,2-dichloroethylene, ethylidene dichloride, methyl chloroform, ethylene dichloride, and trichloroethylene (Johnson, et al. 1959). These by-products not only carry an environmental constraint but can generate subsequent problems during the separation sequence. The purchase of purified methane makes the process non profitable. Thus the purification of methane becomes a requirement.

Level 3 - Recycle structure (Part B.2.c of methodology): The methane is fed in excess in the reactor to obtain the desired product distribution. This requires the recycling of the excess methane to the reactor. The temperature inside the reactor should be controlled to prevent the pyrolysis reaction to occur, this is usually done through maintaining a low $Cl_2$ / $CH_4$ feed ratio and by recycling some of the chlorinated products continuous stirred tank reactor (CSTR). Another possible alternative includes the use of an isothermal plug flow reactor (PFR).

Level 4 - Separation system (Part B.2.d of methodology): The main difficulty in the separation sequence is due to the removal of hydrogen chloride. In the base case this is done through the absorption with water, which gives further problems in the separation sequence and can decompose the products. The presence of water can also create corrosion problems in streams containing chlorine and hydrogen chloride.

A first alternative consists of performing an initial separation of the reactor outlet stream. The reactor outlet stream is flashed, the vapor stream returned to the reactor, and the liquid stream continues through the separation sequence. The advantage of this alternative is the reduction of the amount of product to be exposed to water.

The second alternative is to substitute the water with another solvent. Forlano (1974) suggests the use of part of the chlorinated hydrocarbons as the solvent to remove the hydrogen chloride. This eliminates the use of water or any external solvent which could further be a waste source. Forlano recommends using 5 to 6 moles of chlorinated hydrocarbons per mole of hydrogen chloride to be removed. For the present study 5.5 moles of methyl chloride per mole of hydrogen chloride was used. In order to satisfy this requirement and to obtain a good absorber performance, it is necessary to introduce fresh methyl chloride into the process. The absorber pressure and methyl chloride flowrate were identified through a sensitivity analysis as the critical variables of the new absorber (see Figures 7.12 and 7.13).

### Hydrochlorination of methanol

The hierarchical procedure used identified the alternative of considering a different chemistry for the production of methyl chloride. The use of the new chemistry has several advantages over the current chemistry: (1) the environmental impact is greatly reduced due to the fact that the only byproduct methyl ether ($C_2H_6O$) is not regulated by the EPA, (2) the use of a cryogenic unit is eliminated reducing the operating costs, (3) to maintain a low

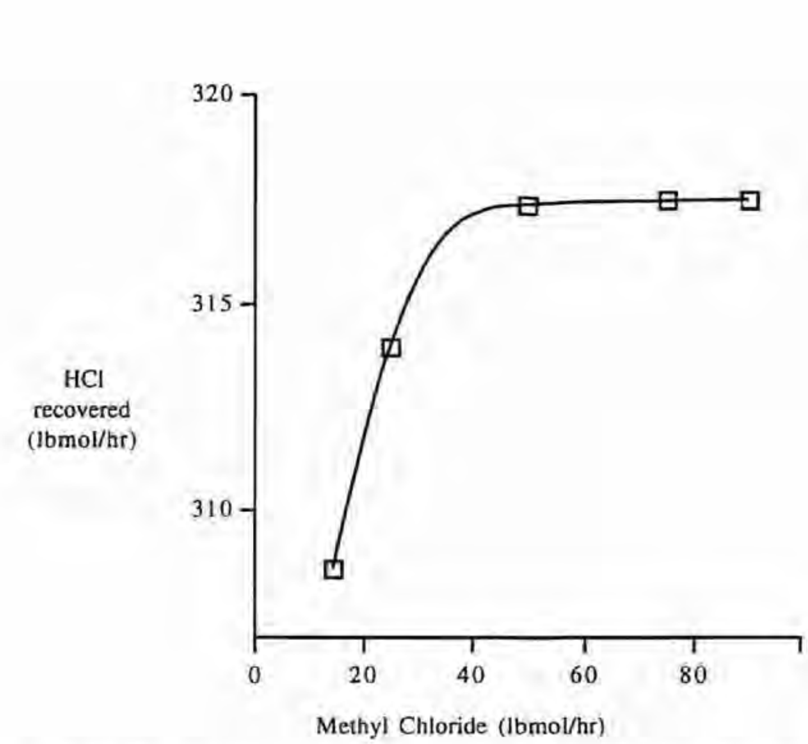

Figure 7.12: Sensitivity analysis for methyl chloride absorber pressure

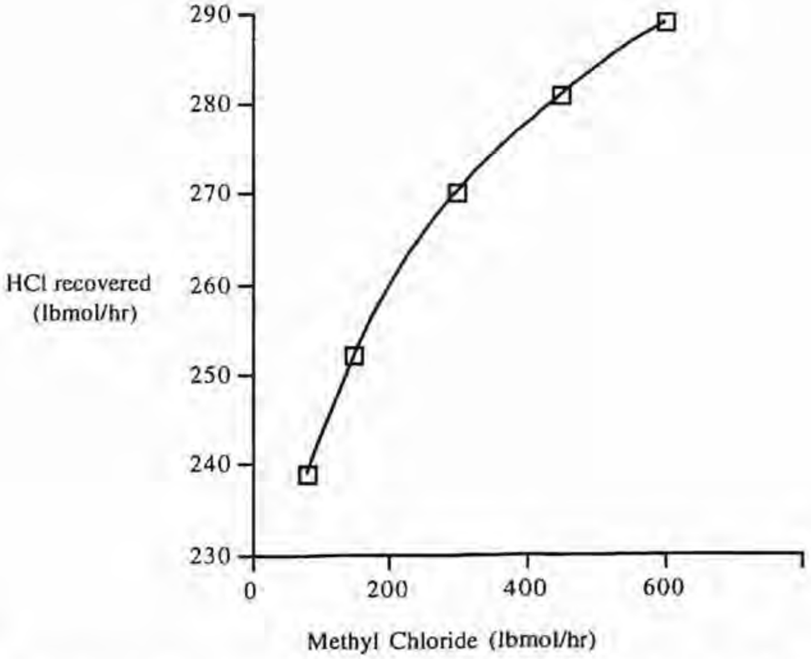

Figure 7.13: Sensitivity analysis for methyl chloride absorber flowrate

byproduct composition, the reactor has to be operated at a very low conversion of methane per pass, thus requiring large volumes of gas to be recycled, and (4) in the thermal chlorination process, big amounts of HCl are produced, unless a good use can be obtained from this byproduct, the HCl may become a burden on the process. The principal drawback in the new chemistry is the increased cost in raw materials.

Although, there exist studies of this new process chemistry, the literature does not report any study for the complete simulation or the economic analysis for the hydrochlorination of methanol. There is also no comparison study between both chemistries. Based on this alternative, the hierarchical procedure is used to evaluate the new chemistry and the possible flowsheet configurations.

Level 1 - Input information (Part B.2.a of methodology): The production of methyl chloride by the hydrochlorination of methanol represents a feasible process alternative. Compared to the thermal chlorination, the hydrochlorination of methanol uses hydrogen chloride as a raw material which is reacted with methanol in the presence of a catalyst (see Scheme II).

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

$$2CH_3OH + HCl \leftrightarrow (CH_3)_2O + H_2O \qquad \text{Scheme II}$$

$$(CH_3)_2O + 2HCl \rightarrow 2CH_3Cl + H_2O$$

The reaction can be carried out using a liquid or a solid catalyst. The solid catalyst system gives a higher throughput per reactor investment than the liquid catalyst system (DeForest 1979). The solid catalyst system operates at 570-660 °F . The possible catalysts include $\gamma$-alumina, silica gel alumina, $ZnCl_2$, $CdCl_2$, $Al_2O_3$, and different zeolites (Becerra, et al. 1992). The use of $\gamma$-alumina has been determined to give a higher conversion (Thyagarajan, et al. 1966). The advantages of this chemistry, is that the environmental impact is reduced due to the existence of only one byproduct methyl ether ($C_2H_6O$), and the reaction to form methyl ether (see Scheme II) does not proceed in measurable quantities (Becerra, et al. 1992). Methyl ether is currently not regulated by the EPA.

The analysis of kinetic data for heterogeneous reactions can be done using either the power law model or the Langmuir-Hinshelwood model. Weller (1956) compares the advantages of using each model. For this study the power law model available in ASPEN PLUS™ was used to represent the solid catalyst system using γ-alumina as the corresponding catalyst. The reported kinetic data (Thyagarajan, et al. 1966) was available in pressure units. To convert to the required units, the data was extracted from the available source, recalculated and replotted. The final form used is shown in Equation 7.7:

$$\begin{aligned} r &= Ae^{-E_a/RT}C_{HCl}C_{CH_3OH} \\ A &= 4.04 \times 10^7 \text{ (sec lbmol/ft}^3)^{-1} \\ E_a &= 38700 \text{ Btu/lbmol} \end{aligned} \tag{7.7}$$

Level 2 - Input output structure of flowsheet (Part B.2.b of methodology): The raw materials used must be of high purity to prolong catalyst life as much as possible. Hydrogen chloride must be purified to remove any impurities, this is usually done through a special purification system to eliminate any chlorinated hydrocarbons.

Level 3 - Recycle structure (Part B.2.c of methodology): Hydrogen chloride is usually fed in excess to reduce the formation of methyl ether. The unreacted hydrogen chloride can be recycled back to the reactor after the removal of water. However, the recovery of hydrogen chloride is difficult since it is at a concentration where an azeotropic mixture is formed with water. The reaction can be carried out in an isothermal or adiabatic PFR reactor. Both alternative reactor systems were considered as possible retrofit alternatives.

Level 4 - Separation system (Part B.2.d of methodology): The reactor effluent is cooled, and separated. The liquid phase containing mostly hydrogen chloride and water is recycled back to the reactor. (Buice, et al. 1987) reports several methods available to accomplish this separation obtaining a 95% recovery of hydrogen chloride. The vapor phase containing mostly methyl chloride is dried with sulfuric acid to remove the remaining amount of water and to eliminate the methyl ether in the final product. The vapor phase purification is similar to the drying step for the thermal chlorination process, and will be evaluated on the amount of water to be removed.

A simulation of the hydrochlorination of methanol process was done using ASPEN PLUS™. Based on the expected separations, both vapor phase and liquid phase purification systems were initially modeled as ASPEN PLUS™ separation blocks (SEP2). The input file for this process is presented in Appendix C.

A sensitivity analysis was performed to identify the variables that affect the performance of the hydrochlorination of methanol. The variables identified were the reactor temperature, condenser temperature, and flash vessel pressure (see Figures 7.14, 7.15, and 7.16).

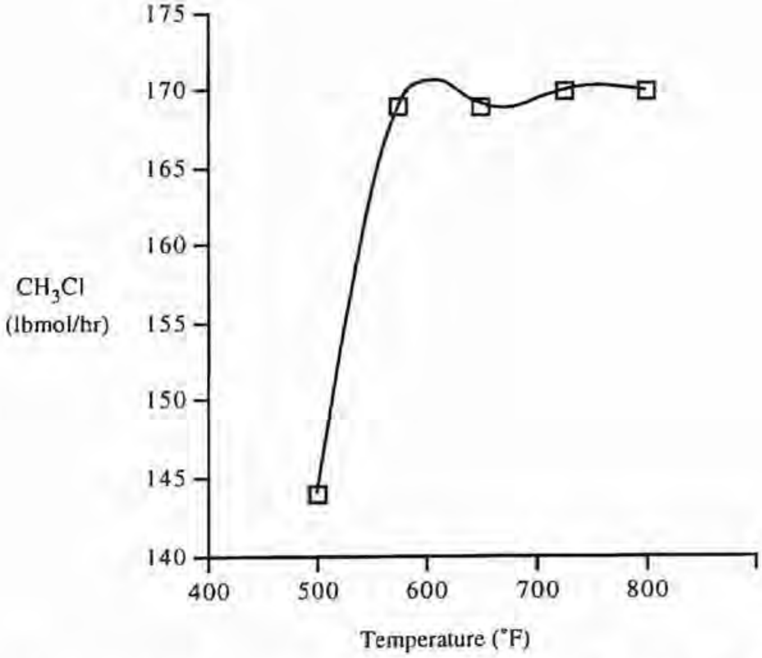

Figure 7.14: Sensitivity analysis for reactor temperature - alternative chemistry

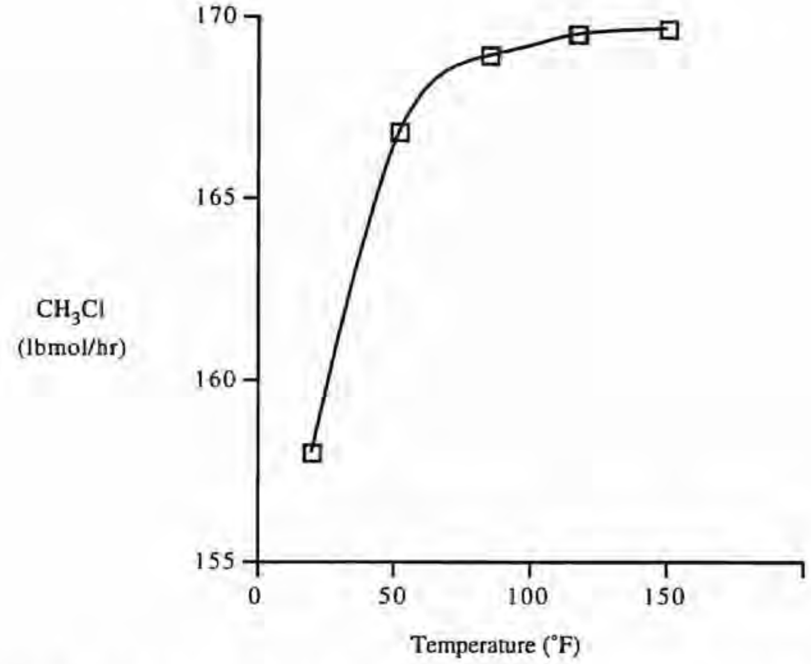

Figure 7.15: Sensitivity analysis for condenser temperature - alternative chemistry

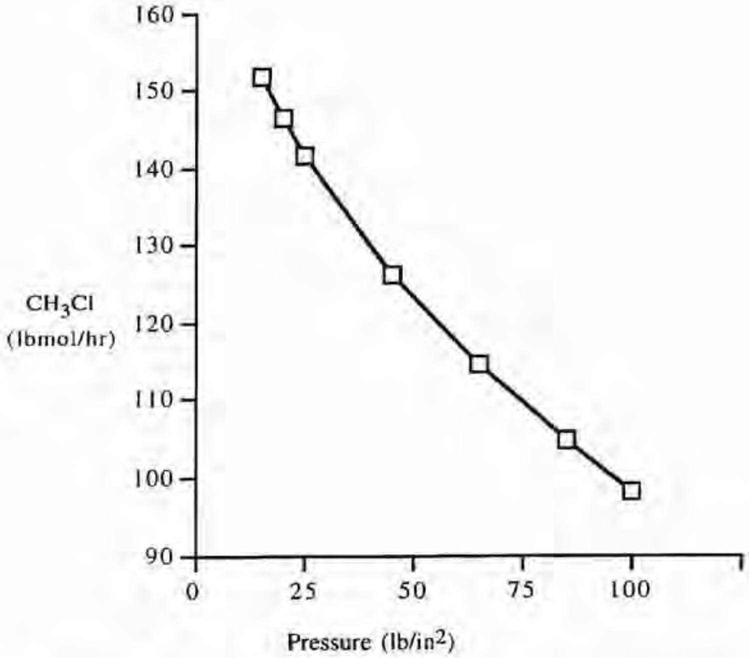

Figure 7.16: Sensitivity analysis for flash vessel pressure - alternative chemistry

## Economic Model for Process Alternatives

The economic model for the process alternatives includes the same data as for the base case. For the case where the effective date of the prices quoted differ from the project date, the values were adjusted using Marshall and Swift equipment cost index (Peters and Timmerhaus 1991). For the new chemistry, the price for methanol is 0.235 $/lb (Chemical Marketing Reporter 1995). The hydrogen chloride feed to the reactor needs to be free of impurities such as water. Thus, both the feed stream and recycle stream have to be purified.

The base case model and retrofit alternatives, did not include rigorous models for the removal of water through NaOH and $H_2SO_4$, as well as the purification of hydrogen chloride and methane. The purification of hydrogen chloride and methane can be considered as separate processes and their operation will depend on the type of unit used and the characteristics of the fresh feed. The fresh feed exiting both purification units is to be considered initially as pure raw materials, and just an economic estimate of their performance was used. The removal of water through NaOH and $H_2SO_4$ was evaluated as a function of the water to be removed. The hydrogen chloride purification presented several problems in the simulation due to the existence of an azeotropic mixture. For the case of sulfuric acid, similar problems were present especially due to difficulties in estimating thermodynamic properties. The rigorous model of these processes should be considered in future research.

Since the separation between water and hydrogen chloride will not be represented with a rigorous model we require some economic data for the comparison of the retrofit alternatives. Zimmer and Guaitella (1976) presents both operating and capital costs required to purify $3 \times 10^7$ $\text{lb}_{\text{waste}}$ / yr. The quoted data has to be adjusted for the required flow of HCl to be purified, the capital costs and operating costs are estimated using Equations 4.9 and 4.10 respectively. The exponent $\psi$ in Equation 4.9 was taken as 0.6.

The capital cost required for each proposed unit is calculated using ASPEN PLUS™ cost estimation blocks. For estimating the cost of vessels, the volume was calculated using the estimated flowrate (see Equations 7.8 to 7.12) (Douglas 1988; Gas Processors Suppliers Association 1994).

$$CF = \left(\frac{M\&S}{280}\right)\left(101.9D^{1.066}L^{0.082}F_c\right) \tag{7.8}$$

$$D = 2\sqrt{\frac{A_v}{\pi}} \tag{7.9}$$

$$L = \frac{4Q_A}{\pi V_t D} \tag{7.10}$$

$$A_v = \frac{Q_A}{V_t} \tag{7.11}$$

$$V_t = K\sqrt{\frac{\rho_l - \rho_g}{\rho_g}} \tag{7.12}$$

where:

$M \& S$ = Marshall & Swift Index

$D$ = Diameter (ft)

$L$ = Length (ft)

$F_c$ = $F_m + F_p$

$F_m$ = Design material factor

$F_p$ = Design pressure factor

$A_v$ = Area of vessel (ft$^2$)

$Q_A$ = Volumetric flowrate (ft$^3$ / sec)

$V_t$ = Terminal gas velocity (ft / sec)

$K$ = Separator sizing factor (ft / sec)

$\rho_l$ = Liquid phase density (lb / ft$^3$)

$\rho_g$ = Gas phase density (lb / ft$^3$)

Gas Processors Suppliers Association (1994) lists values for the separator sizing factor *K*, for different separator types and operating pressures. The separation factor was taken as 0.36 ft / sec, corresponding to an atmospheric pressure operation.

The economic data for each alternative is evaluated based on the Net Present Value method (see Equation 7.13).

$$NPV = \sum_{j=1}^{ny} \left[ f_D \left( \Delta Mc(1 - Tx) + CF * D_j * Tx \right) \right] - CF \tag{7.13}$$

## EVALUATION AND OPTIMIZATION OF PROCESS RETROFIT ALTERNATIVES

This section will present the method to evaluate the previously defined process alternatives and select the best alternative by solving a MINLP problem (Part C of the methodology). The alternatives identified together with the objective function are used to generate a superstructure to evaluate using MINLP and select the optimum flowsheet configuration.

### Formulation of Superstructure

The base case and all the retrofit alternatives are used to formulate an overall flowsheet superstructure (Part C.1 of the methodology) (see Figure 7.17). Figure 7.17 is an ASPEN PLUS™ generated diagram, where each block represents a process unit and each arrow a process stream. The objective function is formulated using the economic model (see Equation 7.12). The continuous variables $x$ were identified through the sensitivity analysis, and the discrete variables $y$ that represent the existence of a specified unit were identified through the hierarchical procedure. The discrete variables were defined using FSPLIT blocks by varying the flow fraction between 0 and 1.

The results obtained from the base case simulation, the simulation of the hydrochlorination of methanol process, and a simulation of each alternative were used as the starting point for the optimization subroutine. Logic constraints were incorporated into the MINLP problem to reduce the number of alternatives to evaluate (Part C.2 of methodology). The superstructure (see Figure 7.17) is simplified by representing the

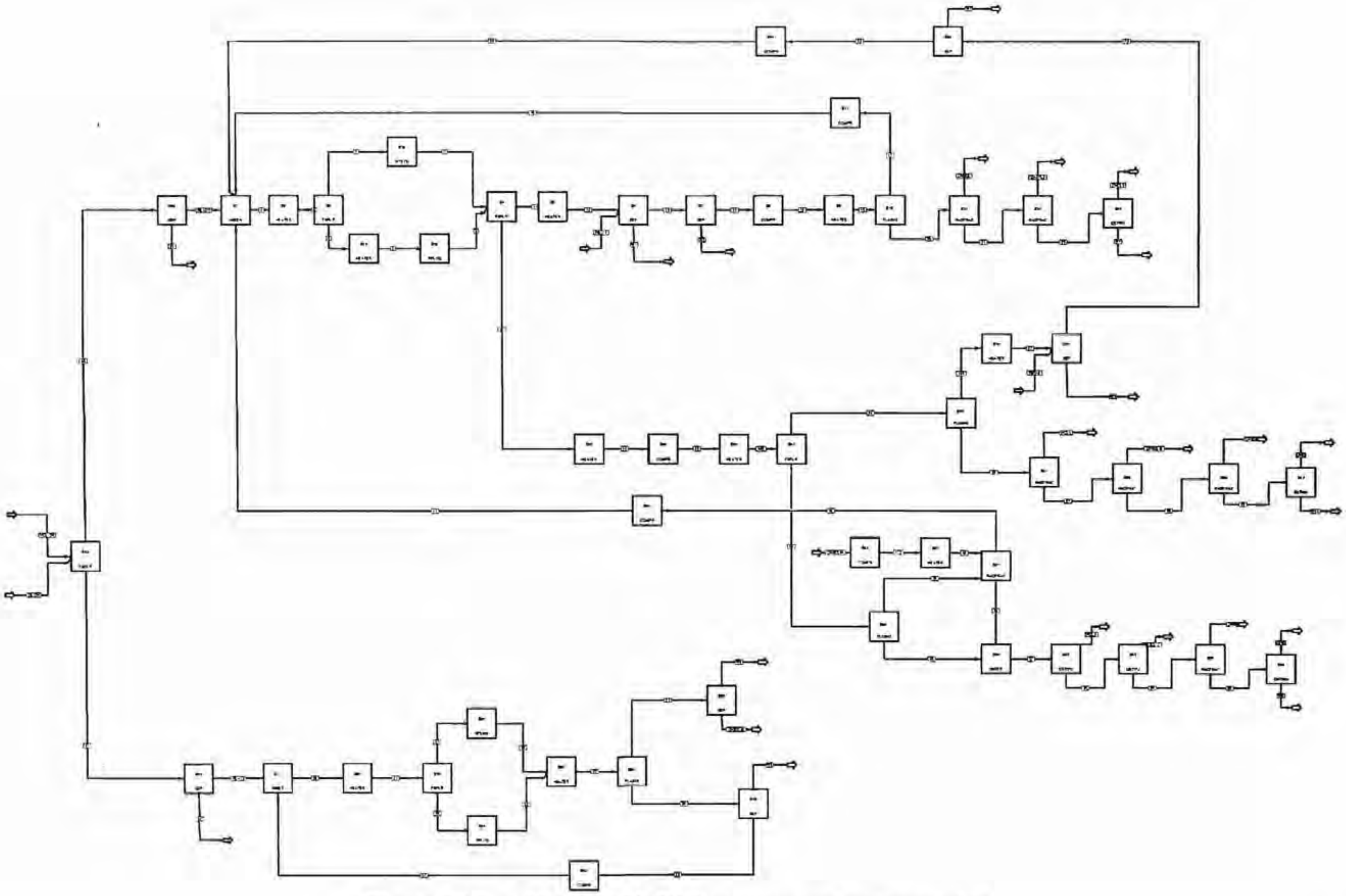

Figure 7.17: ASPEN PLUS™ Superstructure representation

splitters, mixers, input streams, and output streams as Z blocks and the different processing unit sections by Y blocks (see Figure 7.18), where:

Y1 = Initial unit operations for Scheme II
Y2 = Isothermal PFR for Scheme II
Y3 = Adiabatic PFR for Scheme II
Y4 = Separation sequence for Scheme II
Y5 = Initial unit operations for Scheme I
Y6 = Isothermal CSTR for Scheme I
Y7 = Isothermal PFR for Scheme I
Y8 = Initial separation sequence for Scheme I
Y9 = Separation sequence for base case
Y10 = Alternative base case separation sequence (common units)
Y11 = Alternative base case separation sequence with water
Y12 = Alternative base case separation sequence with no water
Z0 = Initial input stream to flowsheet
Z1 = Initial splitter to select between reaction Scheme I and II
Z2 = Splitter to select reactor system for Scheme II
Z3 = Mixer
Z4 = Output stream for Scheme II
Z5 = Splitter to select reactor system for Scheme I
Z6 = Mixer
Z7 = Splitter to select between base case separation sequence and alternative separation sequences
Z8 = Output stream for base case
Z9 = Splitter to select between alternative base case separation sequence with or without water
Z10 = Output stream for alternative base case separation sequence with water
Z11 = Output stream for alternative base case separation sequence with no water

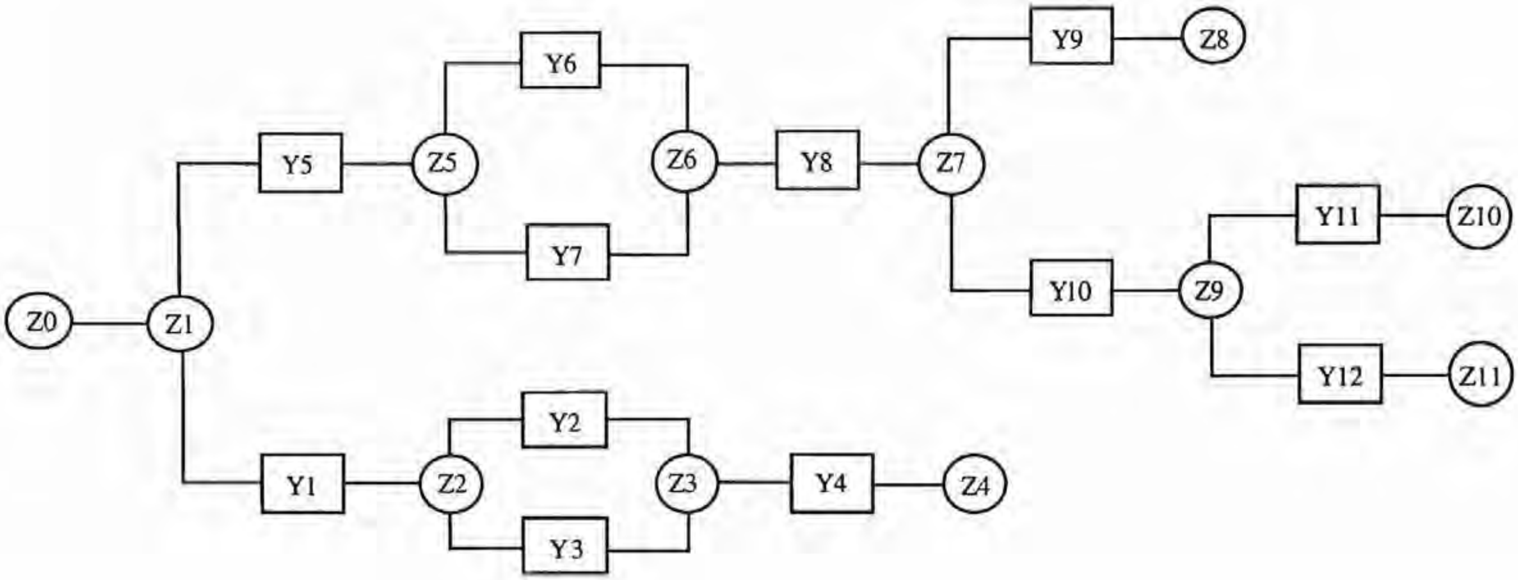

Figure 7.18: Logic representation of superstructure

The logic constraints (see Equation 7.14)

$$\begin{array}{l} Y_1 \vee Y_5 \\ Y_1 \Leftrightarrow Y_2 \vee Y_3 \\ Y_5 \Leftrightarrow Y_6 \vee Y_7 \\ Y_5 \Leftrightarrow Y_9 \vee Y_{10} \\ Y_{10} \Leftrightarrow Y_{11} \vee Y_{12} \end{array} \tag{7.14}$$

are formulated by using Boolean decision variables and the logic representation of the superstructure (see Appendix A).

The final MINLP problem consists of 9 continuous variables,

- Scheme I
  - Methane fresh feed rate
  - Reaction temperature
  - Reaction pressure
  - Compressor outlet pressure
  - Methyl chloride absorber pressure
- Scheme II
  - Hydrogen chloride fresh feed rate
  - Reaction temperature
  - Condenser outlet temperature
  - Flash vessel pressure

10 discrete variables (see Figure 7.18),

- Scheme I
  - Scheme I ($Y_5$)
  - Isothermal CSTR ($Y_6$)
  - Isothermal PFR ($Y_7$)
  - Base case separation sequence ($Y_9$)
  - Alternative separation sequence ($Y_{10}$)
  - Alternative separation sequence with water ($Y_{11}$)
  - Alternative separation sequence no water ($Y_{12}$)
- Scheme II

Scheme II ($Y_1$)

Isothermal PFR ($Y_2$)

Adiabatic PFR ($Y_3$)

and 14 constraints.

$$f_{CH_3Cl-Y_8} + f_{CH_3Cl-Y_{10}} + f_{CH_3Cl-Y_{11}} + f_{CH_3Cl-Y_4} = 160$$
$$Y_1 + Y_5 \geq 1$$
$$Y_1 - Y_2 - Y_3 \leq 0$$
$$Y_2 - Y_1 \leq 0$$
$$Y_3 - Y_1 \leq 0$$
$$Y_5 - Y_6 - Y_7 \leq 0$$
$$Y_6 - Y_5 \leq 0$$
$$Y_7 - Y_5 \leq 0$$
$$Y_5 - Y_9 - Y_{10} \leq 0$$
$$Y_9 - Y_5 \leq 0$$
$$Y_{10} - Y_5 \leq 0$$
$$Y_{10} - Y_{11} - Y_{12} \leq 0$$
$$Y_{11} - Y_{10} \leq 0$$
$$Y_{12} - Y_{10} \leq 0$$

The first constraint specifies the required production rate of methyl chloride of 160 lbmol/hr. The last 13 constraints are obtained by the transformation of Equation 7.14.

This chapter presented the application of the proposed methodology to the production of methyl chloride. The chapter consisted of the development of the base case model, the selection of the process alternatives, and the formulation of the superstructure. The next chapter will present the results obtained by optimizing the superstructure, followed by a process integration study on the selected process configuration.

# CHAPTER VIII

# RESULTS

The production of methyl chloride through the thermal chlorination of methane was used to evaluate the proposed methodology. The methodology developed consisted of four general steps: (1) Development of base case model, (2) generation of process retrofit alternatives, (3) evaluation and optimization of process alternatives, and (4) evaluation of future scenarios. The methyl chloride process was selected because of the environmental constraints and the potential for improvement. The base case model assumed for the current process performance was taken from AIChE Student Contest Problem (1964), and was modeled using ASPEN PLUS™. The input and output data corresponding to the base case process is presented in Table 8.1 and Table 8.2 respectively. The tabulated values correspond to a basis of 8150 hr/yr (Douglas 1988).

Table 8.1: Base Case Input

| Variable | Value |
|---|---|
| Molar feed ratio ($Cl_2$ / $CH_4$) | 0.3 |
| Reactor type | Isothermal CSTR |
| Reaction temperature | 842 °F |
| Reactor effluent cooling system | 77 °F |
| Condenser temperature | -58 °F |
| Compressor outlet pressure | 115 lb/in$^2$ |
| Product demand | $6.59 \times 10^7$ lb/yr |

Table 8.2: Base Case Results

| Variable | Value |
|---|---|
| Methyl chloride flowrate | $6.59 \times 10^{7}$ lb/yr |
| Waste | $3.72 \times 10^{8}$ lb/yr |
| Cooling water requirements | $1.85 \times 10^{11}$ Btu/yr |
| Refrigerant system requirements | $7.41 \times 10^{10}$ Btu/yr |
| Hot utility requirements | $1.23 \times 10^{11}$ Btu/yr |
| Electricity requirements | $1.91 \times 10^{10}$ Btu/yr |
| Manufacturing costs | $1.141 \times 10^{8}$ \$/yr |

The byproducts obtained in a process may in some cases be considered as a revenue, but this might change in the future. To overcome this uncertainty, the byproducts methylene chloride, chloroform, and carbon tetrachloride were not used as a source of revenue. These byproducts were considered as wastes due to the trend in environmental regulations and to penalize the objective function. The evaluation on the effect of this assumption is presented in the next section.

A sensitivity analysis for the base case identified the mole feed ratio, the reactor temperature, the reactor pressure, and the compressor outlet pressure, as potential adjustable variables that can impact the amount of waste generated (see Figures 7.2, 7.5 to 7.11). Different levels of capital cost were considered through the analysis of possible flowsheet configurations. These configurations were identified through a hierarchical procedure. The hierarchical procedure was used to identify the following possible flowsheet configurations:

1. Alternative reaction scheme (Scheme II - Hydrochlorination of methanol)
2. Initial separation of reactor effluent before absorber unit
3. Water replacement in absorber unit
4. Alternative reactor system

The alternatives selected were used to construct a superstructure (see Figure 8.1).

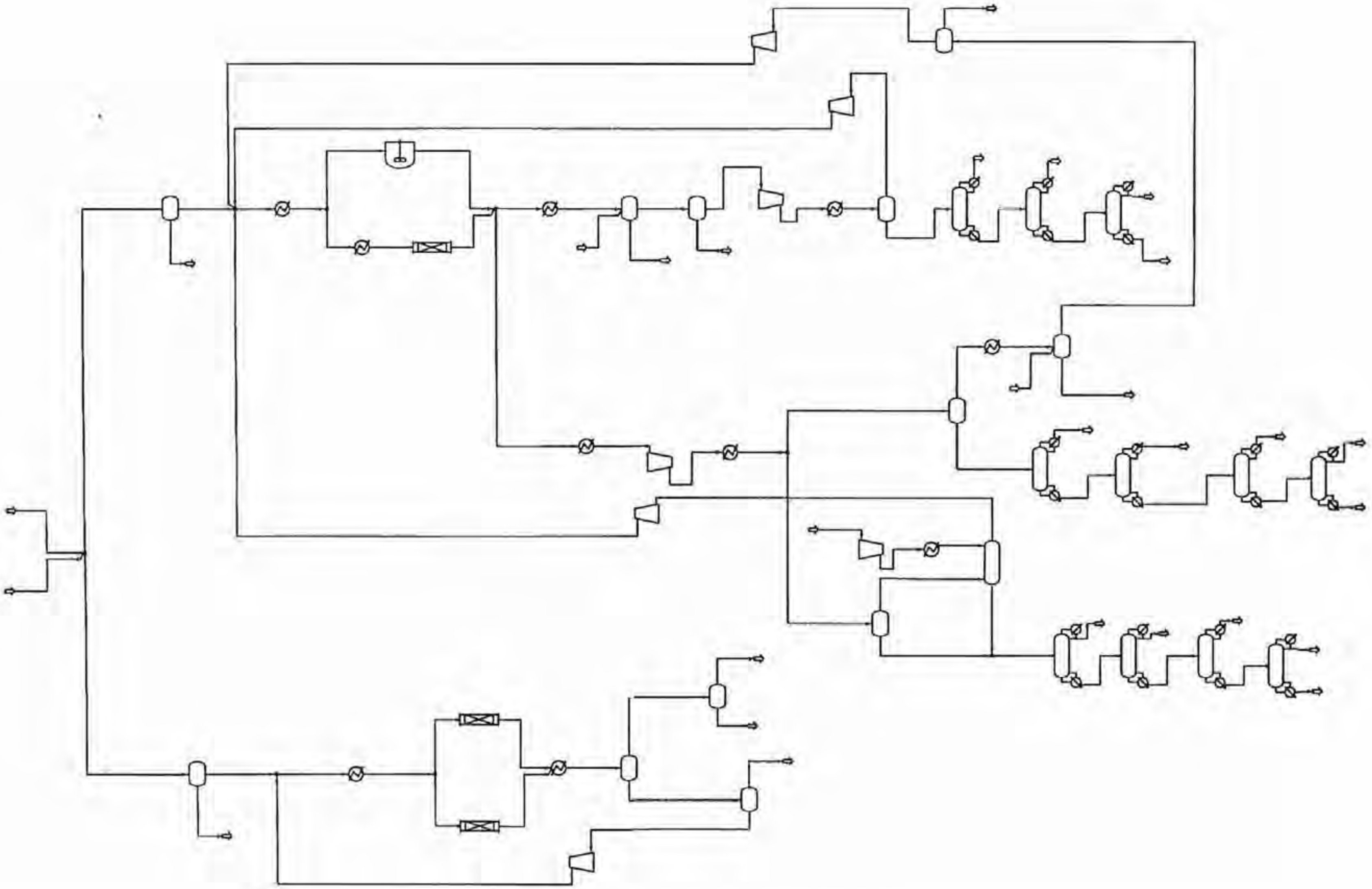

Figure 8.1: Superstructure representation

The superstructure was evaluated using ASPEN PLUS™ by comparing the performance of each alternative to the base case. This comparison is made using the NPV method (see Equation 8.1).

$$NPV = \sum_{j=1}^{ny}\left[ f_D\left( \Delta Mc(1-Tx) + CF * D_j * Tx \right)\right] - CF \qquad (8.1)$$

### Solution of MINLP problem
### (Step C.3 of methodology)

A simulation for each alternative was performed to use as the initial guess for the optimization subroutine, and to formulate the MINLP problem. The MINLP problem consisted of an objective function (see Equation 8.1), 9 continuous variables, and 10 discrete variables (See Figure 8.2 and Table 8.3).

The ranges for most of the variables were obtained from the literature. The change in molar feed ratio was obtained by varying the recycle streams, and the methane and hydrogen chloride fresh feed. For both reaction schemes the limiting reactant fresh feed was fixed to 331 lbmol/hr and 180 lbmol/hr of chlorine and methanol respectively. The discrete variables are identified according to Figure 8.2 and consist of a variation of the fraction flow. The fraction flow will have a value of 1 to represent the existence of a specific unit or process, and a value of 0 to represent the absence of the specific unit or process.

To be able to adequately compare each alternative, the profit calculated corresponded to a fixed product demand of 160 lbmol/hr. This constraint estimates the cost of each alternative, in order to produce the same amount of product, thus making the comparison between alternatives realistic.

The product demand fixes the possible methane and hydrogen chloride fresh feed range that can be introduced into the flowsheet for the reaction scheme I and II respectively. An analysis to evaluate the effect of fresh feed in the objective function is presented in Figures 8.3 and 8.4. This analysis was made by fixing the parameter under study and

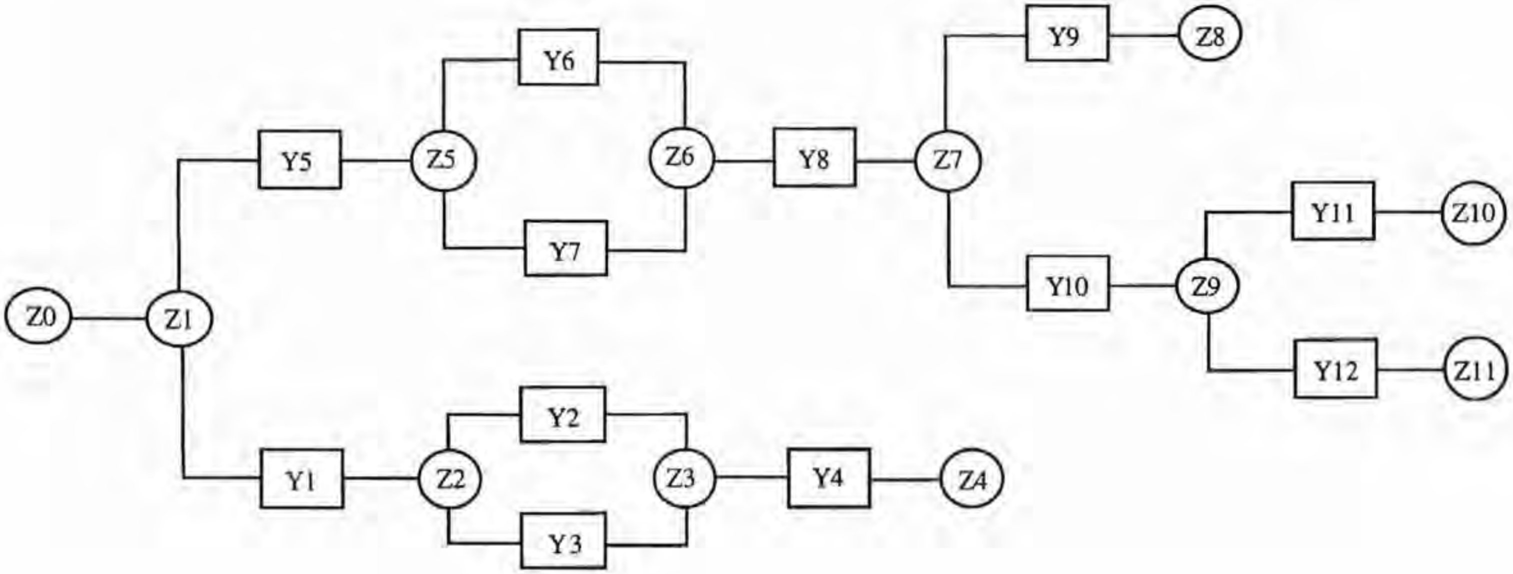

Figure 8.2: Logic representation of superstructure

Table 8.3: Optimization Variables

| Variable | Range |
|---|---|
| Continuous variables (Scheme I) | |
| Methane fresh feed | 270 - 330 lbmol/hr |
| Reaction temperature | 662 - 932 °F |
| Reaction pressure | 14.7 - 73.5 lb/in$^2$ |
| Compressor outlet pressure | 30 - 220 lb/in$^2$ |
| Methyl chloride absorber | 14.7 - 70 lb/in$^2$ |
| Discrete variables (Scheme I) | |
| Scheme I ($Y_5$) | 0, 1 |
| Isothermal CSTR ($Y_6$) | 0, 1 |
| Isothermal PFR ($Y_7$) | 0, 1 |
| Base case separation sequence ($Y_9$) | 0, 1 |
| Alternative separation sequence ($Y_{10}$) | 0, 1 |
| Alternative separation sequence with water ($Y_{11}$) | 0, 1 |
| Alternative separation sequence no water ($Y_{12}$) | 0, 1 |
| Continuous variables (Scheme II) | |
| Hydrogen chloride fresh feed | 190 - 205 lbmol/hr |
| Reaction temperature | 500 - 700 °F |
| Condenser outlet temperature | 30 - 150 °F |
| Flash vessel pressure | 14.7 - 75 lb/in$^2$ |
| Discrete variables (Scheme II) | |
| Scheme II ($Y_1$) | 0, 1 |
| Isothermal PFR ($Y_2$) | 0, 1 |
| Adiabatic PFR ($Y_3$) | 0, 1 |

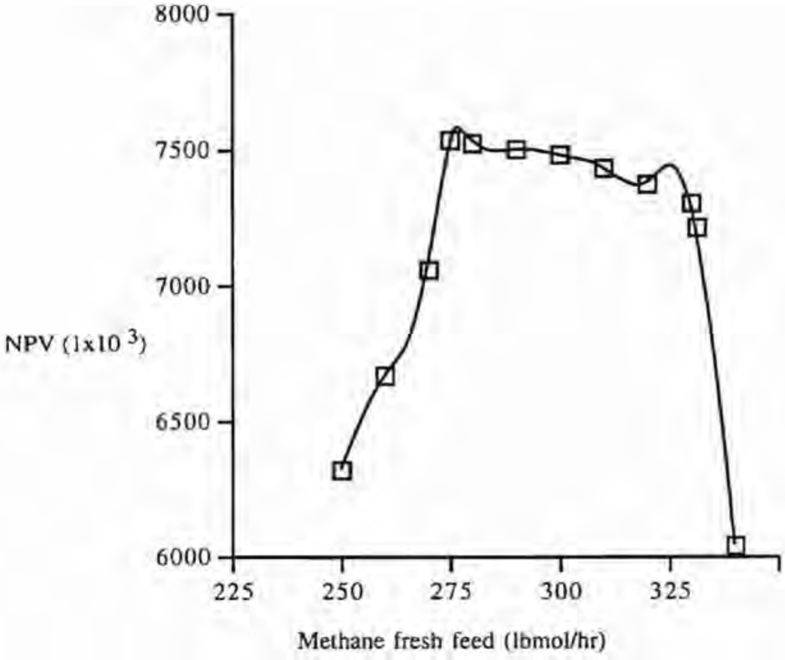

Figure 8.3: Effect of fresh methane feed - Scheme I

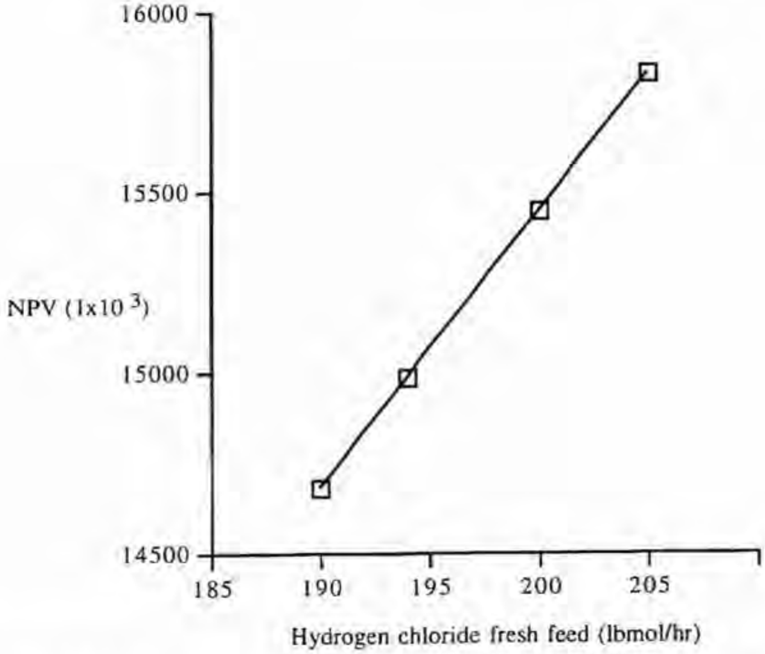

Figure 8.4: Effect of fresh hydrogen chloride feed - Scheme II

varying the remaining variables to maximize the objective function. Outside of the values that were evaluated, the optimization problem does not converge.

The superstructure was composed of three different sections: (1) Base case alternatives, keeping the water as the absorbing agent, (2) Base case alternatives using methyl chloride as the absorbing agent, and (3) Hydrochlorination of methanol alternative process. Due to the differences in these sections and to reduce the size of the MINLP problem, the superstructure input file was divided in three sections (see Appendix D, E, and F):

Section I (see Figure 8.5 and Appendix D): Consists of the base case alternatives for reaction Scheme I. The feed to the reactor considers the possibility of using a CSTR or a PFR. The stream leaving the reactor can continue with the base case separation sequence, or the alternative sequence that considers an initial separation of the product stream before the absorber unit.

Section II (see Figure 8.6 and Appendix E): Also considers the reaction Scheme I. The feed to the reactor can select between a CSTR or a PFR. The stream exiting the reactor is cooled and compressed. The cooled stream is flashed. The vapor stream is passed through an absorber using methyl chloride as the absorbing agent. The liquid stream is passed to a distillation system where the product and byproducts are separated.

Section III (see Figure 8.7 and Appendix F): Consists of the process alternatives for reaction Scheme II. The feed to reactor considers the use of an adiabatic PFR or an isothermal PFR. The reactor outlet is passed through the separation sequence obtaining the desired product.

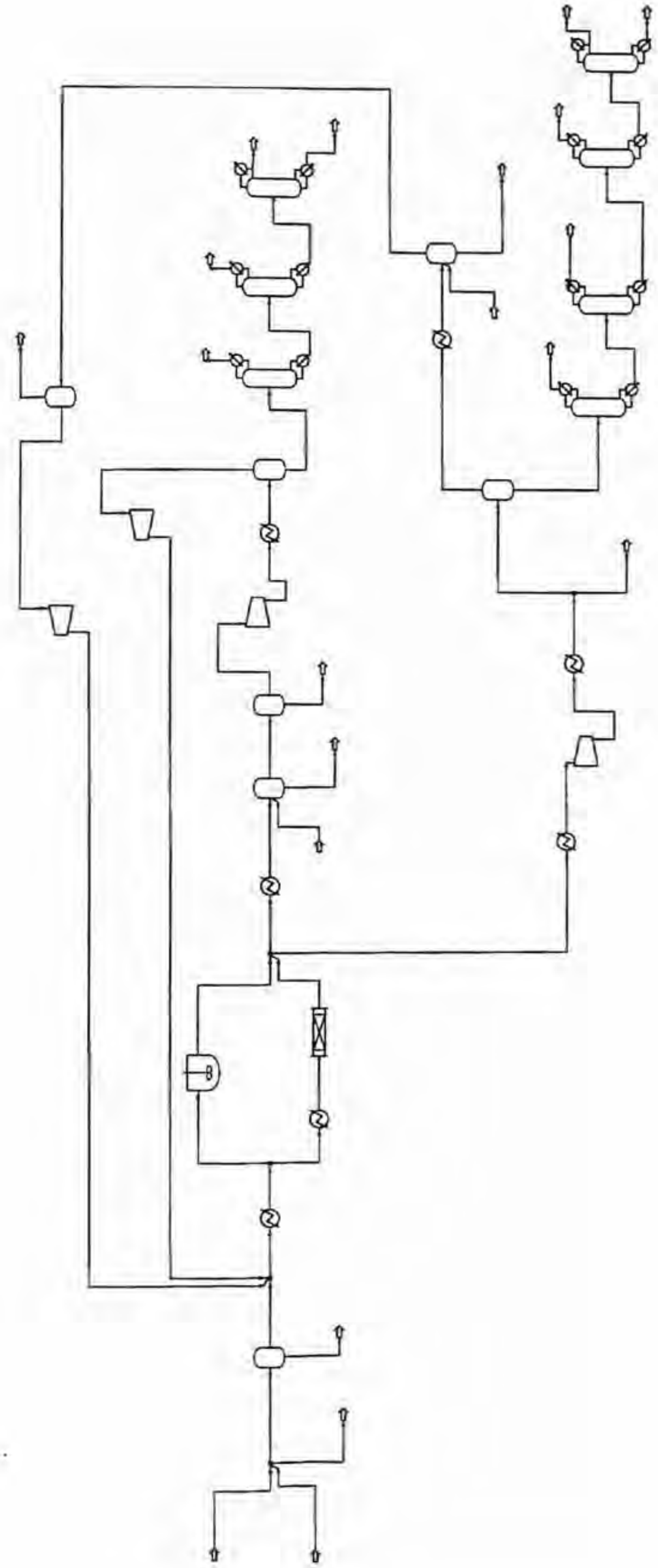

Figure 8.5: Section I

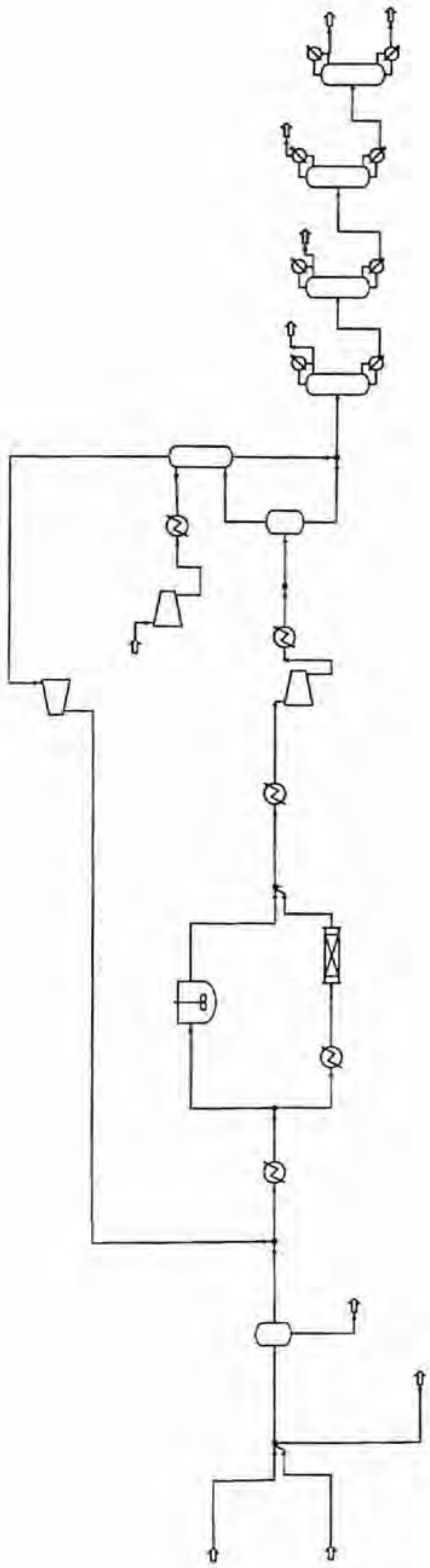

Figure 8.6: Section II

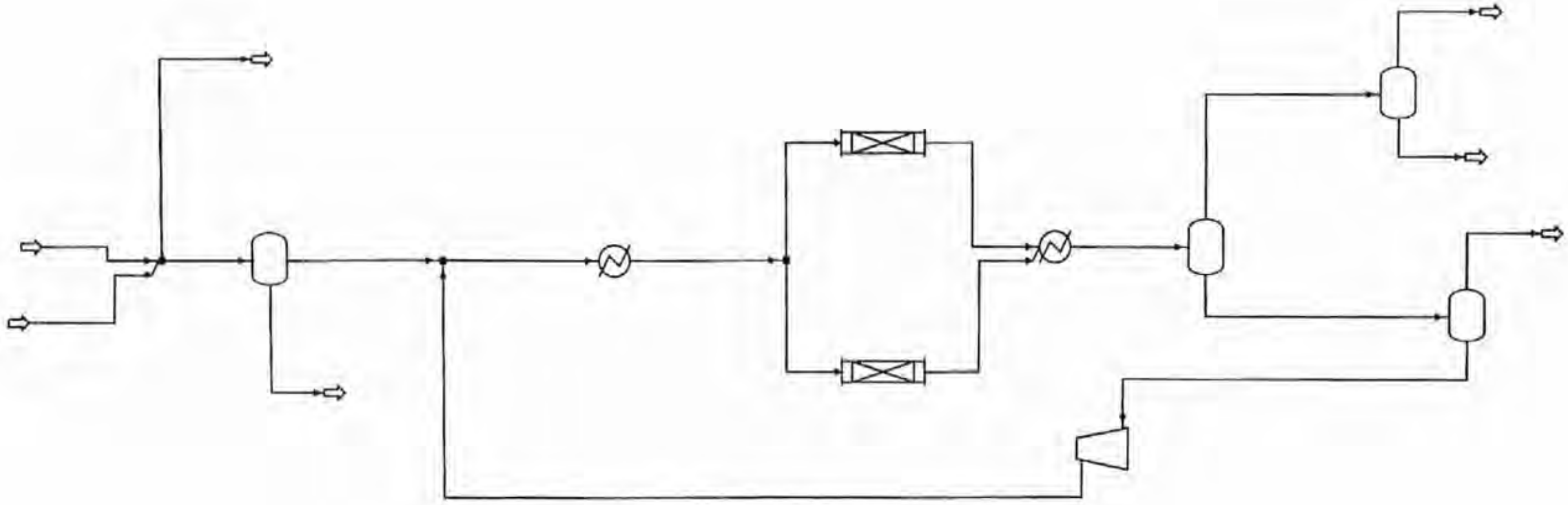

Figure 8.7: Section III

The MINLP problem was solved using a modified algorithm based on the LP/NLP algorithm (Quesada and Grossman 1992). The algorithm was modified to include logic constraints and the use of the disjunctive normal form approach (DNF) to determine the next unit to be branched as well as additional units to be fixed (see Table 6.1 and Appendix A).

The first step in the MINLP procedure requires the establishment of a fixed set of variables $y^l$, this set will determine the upper bound to the solution. The selected set should give a good estimate of the optimum point in order to reduce the number of MINLP iterations. For this case, the base case was selected as the initial set. By varying the specified continuous variables (see Table 8.3), the base case was optimized. The first attempt to optimize did not converge when varying the fresh feed of methane. Even though the feed was varied according to the calculated ranges, the objective function (see Figure 8.3) may present discontinuities over that range. Based on Figure 8.3, the methane feed was fixed at 175 lbmol/hr, which represents the optimum point. This value was further increased to 180 lbmol/hr in order for the isothermal PFR to converge to the specified production demand. For Section II of the superstructure containing the alternative separation sequence with no water, the range of methane fresh feed was increased to 440-475 lbmol/hr, to satisfy production demand. The differences in the ranges used for the methane feed were also an important factor in considering the separation of the superstructure in three sections.

The operating pressure for the absorber using methyl chloride as the absorbing agent also presented discontinuity problems. As expected, the increase in the absorber pressure lowers the profit (see Figure 8.8). The values presented in Figure 8.8 were obtained by fixing the parameter under study and varying the remaining variables to maximize the objective function. Figure 8.8 presents a strange behavior in the objective function. Although more points were evaluated between the ranges of 15 to 30 and 30 to 40 lb/in$^2$, the optimization subroutine did not converge. To overcome these problems and based in Figure 8.8 the absorber was fixed to work at atmospheric pressure.

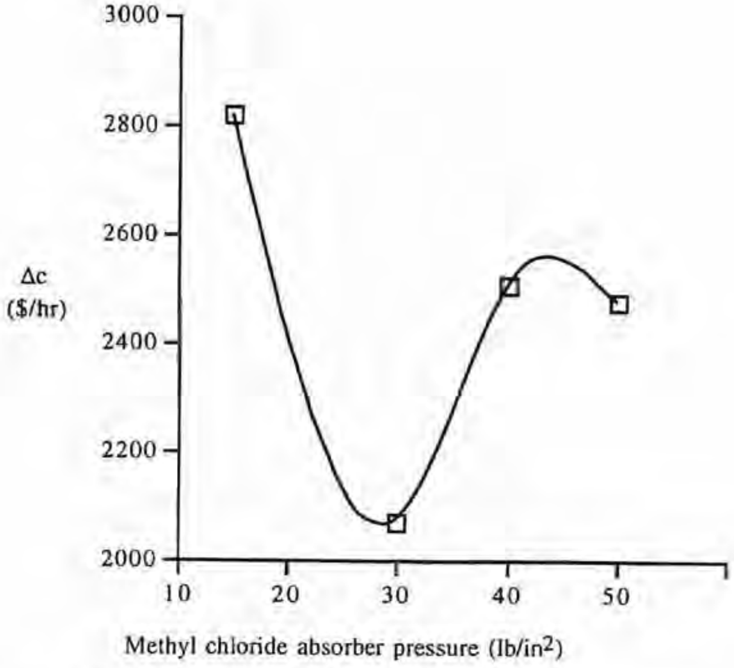

Figure 8.8: Effect of methyl chloride absorber pressure

The upper bound to the MINLP problem corresponds to the optimization of the base case (see Table 8.4). This represents results that can be obtained with the existing processes without any major capital investment. The results described in Table 8.4 consider the byproducts methylene chloride, chloroform, and carbon tetrachloride as wastes. Although these products can represent a profit to the actual process, they were considered as wastes due to the trend in environmental regulations and to penalize the objective function. Is important to notice that when we compare the results from Table 2 (base case results) against the results from Table 8.4 (base case optimization results), we see a decrease in the waste generated, but an overall increase in utility costs. These costs will be reduced when heat integration is applied.

The superstructure is comparable in size to reported cases in the literature (Diwekar, et al. 1992a; Diwekar, et al. 1992b). The superstructure was evaluated in 160 minutes of CPU time using a modified algorithm based on the LP/NLP algorithm (Quesada and Grossman 1992) (see Table 6.1 and Appendix A). The CPU time required appears to be greater than reported cases. The reported CPU times available are for the case of equation based simulators, however care must be taken when comparing performance of different MINLP problems and different process simulators.

Table 8.4: Base Case Optimization Results

| Variable | Value |
|---|---|
| Net present value | \$ $7.528 \times 10^6$ |
| Molar feed ratio to reactor ($Cl_2$ / $CH_4$) | 0.101 |
| Methane fresh feed | 280 lbmol/hr |
| Reaction temperature | 663.3 °F |
| Reaction pressure | 14.7 $lb/in^2$ |
| Compressor outlet pressure | 139.7 $lb/in^2$ |
| Waste | $2.21 \times 10^8$ lb/yr |
| Cooling water requirements | $2.61 \times 10^{11}$ Btu/yr |
| Refrigerant system requirements | $1.66 \times 10^{11}$ Btu/yr |
| *Hot utility requirements* | $2.80 \times 10^{11}$ Btu/yr |
| Electricity requirements | $4.43 \times 10^{10}$ Btu/yr |

The final results for each subsection of the superstructure are shown in Table 8.5. The capital costs in Table 8.5 represent the worst case scenario where the possibility of using the existing process equipment for the process alternatives is not considered, since no equipment specifications are available for the current process. The existing equipment might be compatible with a process alternative, thus reducing the capital costs required. Analyzing the results presented in Table 8.5, the optimum flowsheet configuration corresponds to the hydrochlorination of methanol by using an adiabatic PFR. This alternative considers the case of completely replacing the current process. Even though this alternative requires high investment costs, an increase in savings for both operating costs and waste disposal costs, makes this a feasible alternative.

Table 8.5: MINLP Results for Superstructure

| Variable | Final value |
|---|---|
| Section I (Scheme I, base case and alternative separation sequence) | |
| Net present value | \$ 7.53 x $10^6$ |
| Capital cost | \$ 0 |
| Isothermal CSTR ($Y_6$) | 1 |
| Isothermal PFR ($Y_7$) | 0 |
| Base case separation sequence ($Y_9$) | 1 |
| Alternative separation sequence ($Y_{10}$) | 0 |
| Alternative separation sequence with water ($Y_{11}$) | 0 |
| Section II (Scheme I, separation sequence with no water) | |
| Net present value | \$ 3.43 x $10^6$ |
| Capital cost | \$ 6.34 x $10^6$ |
| Isothermal CSTR ($Y_6$) | 1 |
| Isothermal PFR ($Y_7$) | 0 |
| Section III (Scheme II) | |
| Net present value | \$ 14.6 x $10^6$ |
| Capital cost | \$ 10.4 x $10^6$ |
| Isothermal PFR ($Y_2$) | 0 |
| Adiabatic PFR ($Y_3$) | 1 |

The best alternative for reaction Scheme I, corresponds to the optimization of the base case. As was mentioned previously this considers a penalty for the production of methylene chloride, chloroform, and carbon tetrachloride. If we do not penalize the objective function, the new NPV calculated is \$7.82 x $10^6$. If we compare this value against the hydrochlorination of methanol (see Table 8.5), the latter still represents the best alternative. But since a certain revenue can still be obtained from these byproducts, a comparison between short term and long term effects should be made to determine the flowsheet configuration to be selected. Considering the trend in environmental constraints the present study will take the hydrochlorination of methanol as the selected flowsheet configuration (see Table 8.6).

Table 8.6: Hydrochlorination of Methanol Optimization Results

| Variable | Final value |
|---|---|
| Hydrogen chloride fresh feed | 5.65 x $10^7$ lb/yr |
| Reaction temperature | 695.6 °F |
| Condenser outlet temperature | 139.3 °F |
| Flash vessel pressure | 41.7 lb/in$^2$ |
| Isothermal PFR ($Y_2$) | 0 |
| Adiabatic PFR ($Y_3$) | 1 |
| Cooling water requirements | 6.07 x $10^{10}$ Btu/yr |
| Hot utility requirements | 4.29 x $10^{11}$ Btu/yr |
| Electricity requirements | 6.64 x $10^6$ Btu/yr |
| Waste | 3.78 x $10^7$ lb/yr |

## Process Integration

The information generated during the optimization block is used to construct the heat exchanger network (HEN) superstructure (Part C.4 of methodology). For the selected flowsheet only one hot stream and one cold stream are considered for the heat integration step. The cold stream is the stream that goes into the reactor, and the hot stream goes to the separation system. Each stream considers a possible match with another stream or the bypass of that match. The heat load not satisfied by the in-process match will be supplied by the corresponding heating and cooling utilities (see Figure 8.9), where:

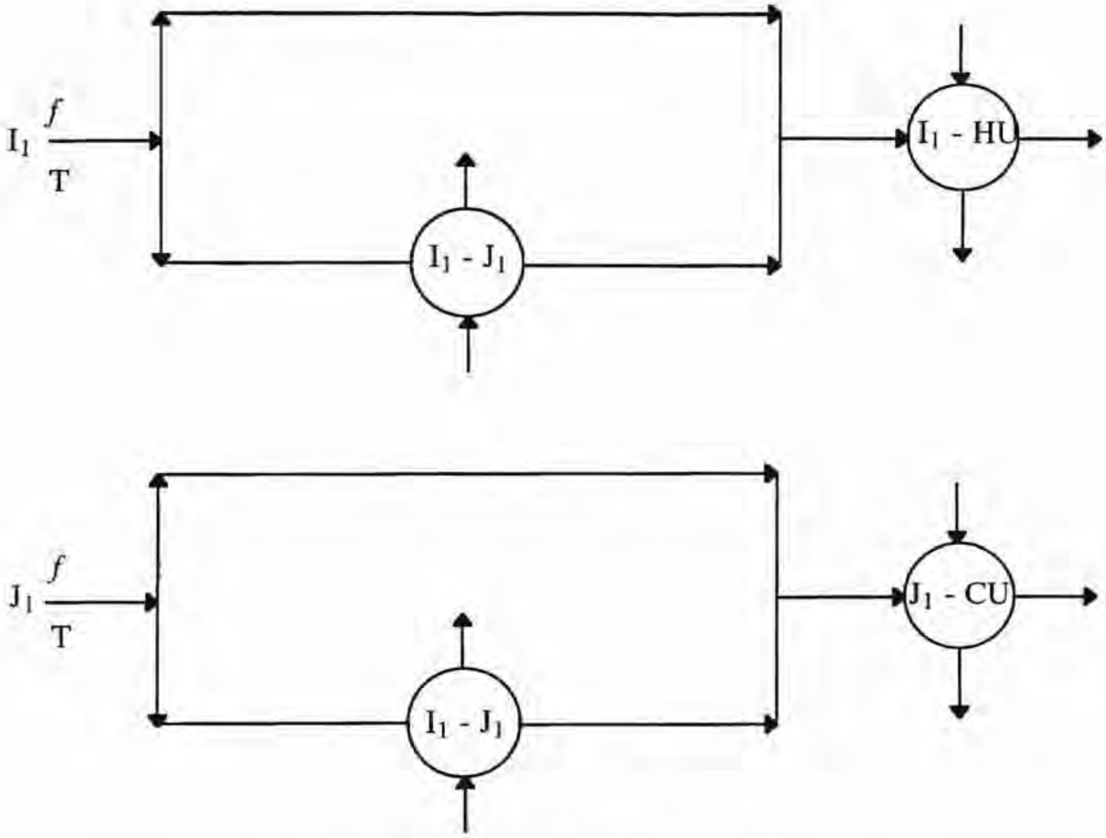

Figure 8.9: Final HEN Superstructure

$f$ = Flowrate

T = Temperature

HU = Hot utility

CU = Cold utility

$I_1$ = Cold stream entering the reactor

$J_1$ = Hot stream entering the separation system

$I_1$ - $J_1$ = Heat exchanger between streams $I_1$ and $J_1$

$I_1$ - HU = Heat exchanger between stream $I_1$ and HU

$J_1$ - CU = Heat exchanger between stream $J_1$ and CU

The HEN superstructure consists of an objective function (see Equation 8.1 and Figure 8.9) and five constraints corresponding to the specified outlet temperatures, the fixed $\Delta T_{min}$, and the constraint that specifies the possible match. For the present case, stream splitting was allowed. The input file is presented in Appendix G. The solution of the HEN superstructure (Part C.5 of methodology) was obtained in 9.53 seconds of CPU time using ASPEN PLUS™. No reported case of using ASPEN PLUS™ to solve a HEN configuration is available in the literature, in order to make a valid comparison.

The heat integration analysis results in the identification of a match between the selected streams. The heat integration requires an external cold utility heat load of 1.74 x $10^{10}$ Btu/yr, and no more hot utilities are needed. This represents a reduction in utility requirements, as well as an additional saving in the operating costs and a reduction in the emissions associated with the use of process utilities.

The final flowsheet for the hydrochlorination of methanol is presented in Figure 8.10. This flowsheet incorporates the optimum configuration from the process and HEN superstructure. The methanol and hydrogen chloride feed to reactor is heated to 696 °F. The stream is introduced to an adiabatic PFR, where reaction Scheme II takes place. The reactor effluent is cooled to 139 °F using the reactor feed stream and the cold utilities. The cooled stream is compressed to 41.7 lb/in$^2$ and flashed. The vapor stream is purified to

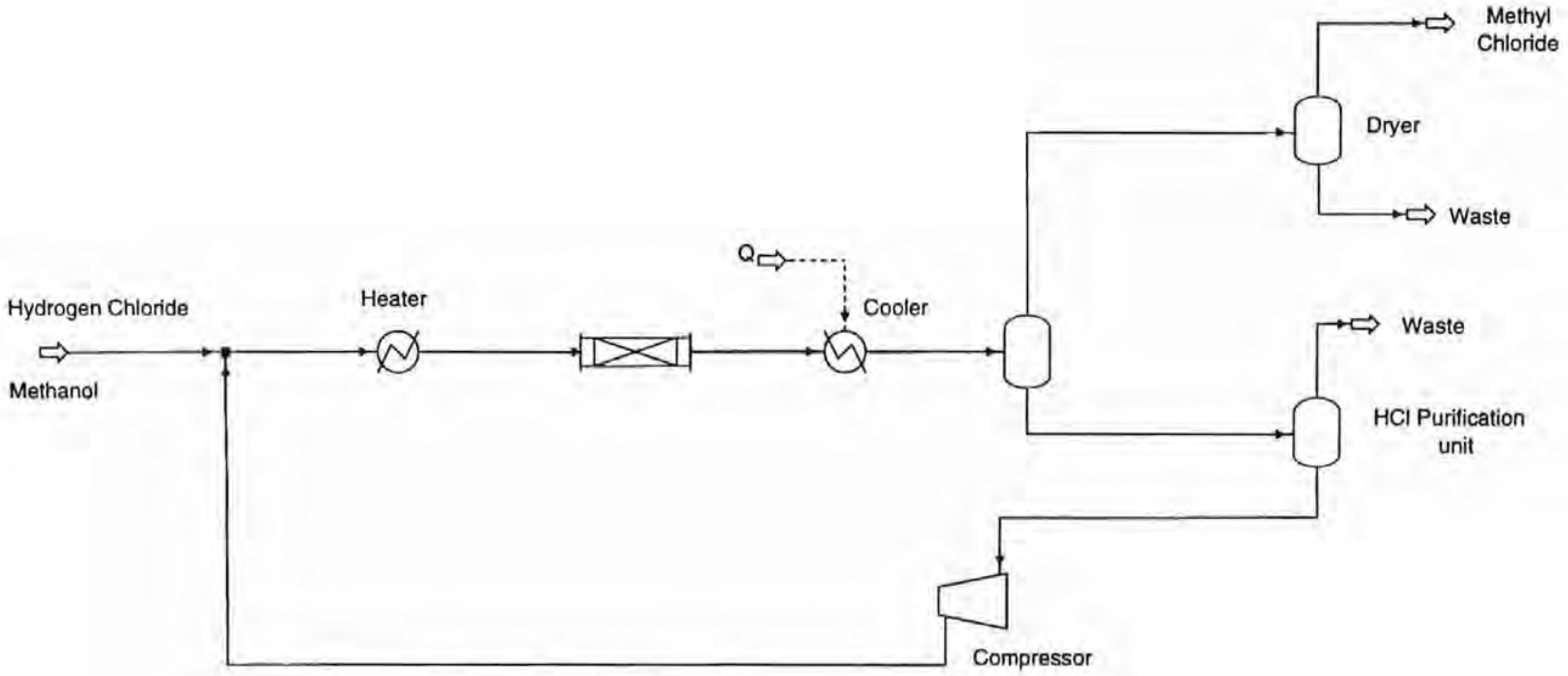

Figure 8.10: Final Flowsheet

remove the remaining water from the product stream. The liquid stream is purified to recycle the excess hydrogen chloride back to the reactor.

## Future Scenarios

An analysis on the effect of waste costs shows that this was a critical factor in the selection of the optimal flowsheet. The economic model used assumed the byproducts as wastes, even though revenue can be obtained from them, and a demand still exists for these products. The optimization of the superstructure without considering the byproducts as wastes, still identifies the hydrochlorination of methanol as the best alternative. There are reported cases in the literature (Deforest 1979) where in order to reduce raw material requirements a combined process uses both the thermal chlorination of methane and the hydrochlorination of methanol. The hydrogen chloride produced in the Scheme I is used as a raw material in Scheme II. This alternative reduces the excess of hydrogen chloride and still has the flexibility of obtaining the different chlorinated hydrocarbons. The combined process might also be a solution in order to obtain a gradual change from one process into the new process.

The economic model did not consider the type of waste or the risk associated with each chemical, and did not consider the possibility of recycling, reusing, regenerating or treating the waste generated. But in any case the increase in amount of waste will be directly related to the operating costs and thus affect the overall profit of the operation. This increase will shift even more the decision regarding the hydrochlorination of methanol, being this a more environmentally friendly process.

Several other factors were not included in the economic model such as safety and operability factors. It was established that the temperature inside the reactor for the thermal chlorination of methane, requires a strict control. A PFR gives the possibility of better temperature control during the reaction than a CSTR. But since the CSTR gives a better product distribution, this type of reactor was chosen over the PFR. The hydrochlorination of methanol process is a safer process. This occurs due to the absence of the reaction temperature restrictions available in the thermal chlorination process. If a strict control of the temperature is not carried out an explosion might occur.

This chapter presented the evaluation of the superstructure that included all the identified retrofit alternatives. To reduce the size of the MINLP problem and due to certain differences between certain alternatives, the superstructure was divided in three sections. The MINLP problem was solved, identifying the hydrochlorination of methanol as the optimum flowsheet configuration. This configuration was evaluated using the process integration approach to determine the optimum HEN configuration.

In summary, the proposed methodology was successfully applied to the production of methyl chloride by the thermal chlorination of methane. The process model was found to behave similarly to published results. The sensitivity study identified as waste reduction variables the reaction temperature, reaction pressure, mole feed ratio, and compressor outlet pressure. The hierarchical procedure identified the use of an alternative chemistry, alternative stripping agent and alternative separation sequence. These waste reduction variables together with the alternatives identified through the hierarchical procedure were incorporated in a superstructure and successfully evaluated using ASPEN PLUS™. The results obtained identified the hydrochlorination of methanol as the best process alternative. The selected alternative compared to the base case process provides a decrease in waste generated and in utility requirements, as well as an overall increase in profit.

# CHAPTER IX

# CONCLUSIONS AND FUTURE DIRECTIONS

## Conclusions

A methodology was developed to retrofit existing processes in the chemical industry. This methodology was aimed at reducing the waste generated at the source and improve the energy consumption, while satisfying all the environmental and product specifications, and remaining profitable. The methodology accomplished the combined use of the three retrofit techniques (1) hierarchical design procedure, (2) pinch technology tools, and (3) mathematical programming methods. Based on these techniques a combined methodology was proposed which consisted of four general steps:

1) Development of base case model
2) Generation of process retrofit alternatives
3) Evaluation and optimization of process alternatives
4) Evaluation of future scenarios

The main tool used in this study was ASPEN PLUS™, a sequential process simulator. The use of dynamic simulators, such as SPEEDUP™, may provide a better representation of the behavior of the process, either continuous or batch, and will be helpful in simulating the startup and shutdown procedures. Even though SPEEDUP™ may be a more powerful tool, it was not available at the time of this research, but will be considered in the future. The black box characteristic of ASPEN PLUS™, has several advantages, but for the present study it presented several limitations, since it was not possible to adequately exchange information between the user and the optimization algorithm. This information is essential if linear approximations are to be included as part of the MINLP - ASPEN environment. This represents an advantage in using equation based simulator such as SPEEDUP™.

In order to successfully apply the ASPEN PLUS™ SQP algorithm, a very good initial guess must be supplied, this requires the user to have a good idea of where the optimum point is located. For the case when such information is not available, several sensitivity-optimization studies are required, such as the ones done for the methane and hydrogen chloride fresh feed flows. These studies are made by fixing the variable under study and optimizing the flowsheet for a specific value of the fixed variable. The optimization of the superstructure requires a lot of time. This was the main reason for separating it in to three sections. As a more accurate model is constructed the required CPU time will increase, and for the case of bigger flowsheets the use of parallel computers may become an option. For this case the different branches in the solution tree could be evaluated in parallel.

Another critical parameter to consider is the number of retrofit alternatives to evaluate. Therefore, the screening procedure should be able to eliminate infeasible retrofit alternatives. For the case of waste minimization, the use of a hierarchical procedure increases the performance of the screening procedure, and helps also in identifying solutions that may have an immediate application.

The final decision criteria used to select a specific process alternative will rely on an economic evaluation of this alternative. The economic model used to evaluate each alternative should took into account the capital and manufacturing costs associated with a specific process. This takes into consideration the fact that the most environmentally friendly process might not be the most economical. The economic tool used to compare process alternatives was the net present value (NPV) method, that represents the best profitability comparison tool (Peters and Timmerhaus 1991).

As the chemical industry is designing new processes or retrofitting existing ones, an evaluation tool is necessary to evaluate the different process alternatives. This tool must include environmental constraints as well as additional economic criteria such as safety, risk, controllability, etc. These criteria becomes important as the waste minimization approach is focused not only on the manufacturing process itself, but on the product life cycle, from raw materials to final disposition (Freeman 1992). The present work represented a starting point for a rigorous economic analysis. Existing methods that focus on environmental issues rely either on simple economic analysis (Douglas 1992; Douglas and Woodcock 1987), or on no economic criteria (Chadha 1994; Karam and Cin 1988; Petrides et al. 1994). These methods are not very rigorous, but give a starting point for the generation of feasible alternatives that can be further analyzed with more complete techniques.

The production of methyl chloride through the thermal chlorination of methane was used as a case study to evaluate the proposed methodology. The methyl chloride process was selected because of the environmental constraints and the potential for improvement. An initial optimization of the existing process yields an increase in profit and decrease in waste generated. This represents results that can be obtained with the existing processes without any major capital investment. After considering the different flowsheet configurations, an optimal flowsheet was selected that corresponds to the hydrochlorination of methanol.

The base case model and retrofit alternatives, did not include rigorous models for the removal of water through NaOH and $H_2SO_4$, as well as the purification of hydrogen chloride and methane. The purification of hydrogen chloride and methane can be considered as separate processes and their operation will depend on the type of unit used and the characteristics of the fresh feed. The fresh feed exiting both purification units is to be considered initially as pure raw materials, and just an estimate of their performance was used in the economic model. The removal of water through NaOH and $H_2SO_4$ was evaluated as a function of the water to be removed. The hydrogen chloride purification presented several problems in the simulation due to the existence of an azeotropic mixture. For the case of sulfuric acid, similar difficulties were present especially due to problems in estimating thermodynamic properties. The rigorous model of these processes should be considered in future research.

The hydrochlorination of methanol process did not include the simulation of methyl ether as an important byproduct. The formation of methyl ether was not included in the model because it does not proceed in measurable quantities and kinetic data was not available. The inclusion of the methyl ether in the model should be consider since this chemical causes subsequent problems in the manufacture of silicones, which is the principal use of methyl chloride.

In summary, the principal contribution of this study was the combination of the retrofit methods to minimize waste and improve energy efficiency. This was done by developing a rigorous economic model that incorporates both fixed capital and operating costs. This model was solved as a MINLP problem using a sequential process simulator ASPEN PLUS™.

In summary the following conclusions can be made:

1) The development of the base case model and the use of negative flowsheets can help identify waste minimization opportunities.
2) ASPEN PLUS™ was used successfully to model the base case process, to model the superstructure and to solve the MINLP problem.
3) The optimum HEN configuration can be obtained by formulating an MINLP representation and solved using ASPEN PLUS™.
4) The critical operating variables for the current process were identified as well as their optimum value.
5) An increase in profit and a reduction in waste generated can be made to the existing process without any major capital investments.
6) Several alternative flowsheet configurations were identified and evaluated using ASPEN PLUS™.
7) The hydrochlorination of methanol was chosen as the best process to meet the specified demands and has a smaller environmental impact.

## Future Directions

As a more general methodology is developed for the chemical processing industry, there is still a great field of research to be conducted. The research directions to be considered in the future are:

1) Develop a more accurate model for waste related costs that will include usual costs, as well as hidden, liability, and less tangible costs.
2) Incorporate the use of approximations to improve the MINLP algorithm performance and reduce the number of iterations required.
3) Incorporate risk, safety, uncertainty and operability criteria in to the evaluation of possible alternatives.
4) Evaluate the possibility of using parallel computers to reduce CPU time, especially as the number of retrofit alternatives is increased.
5) Include layout considerations in implementation of retrofit alternatives. This is especially important in the case of heat integration. The cost of repiping or the physical limitations of possible matches, might be greater than the savings proposed. The use of layout considerations was not used since no data was available regarding the physical placement of process units.
6) Consider the use of SPEEDUP™ for the retrofit of batch processes, and a more accurate representation of the process performance. SPEEDUP™ was not available at the time of this research.
7) Evaluate the use of better SQP algorithms or alternative optimization algorithms.
8) Improve the efficiency of the MINLP-ASPEN algorithm, by including the selection of alternatives as part of the subroutine.
9) Integrate the use of mass exchanger networks (MEN) to consider reuse of waste streams and to improve separation processes. Since the present study was focused primarily on source reduction, the use of MEN was not considered.

Regarding the case study,

1) Develop a rigorous model for the kinetics of the hydrochlorination of methanol that includes the formation of methyl ether as a byproduct. The model used did not consider this chemical, since kinetic data was not available.
2) Construct a more rigorous model regarding the water removal, methane purification, and hydrogen chloride purification.

3) If necessary, evaluate the possibility of using a combined process between both reaction schemes. This completely new process was not considered as an alternative in the present study. The principal advantage of this process, is the reduction of the excess hydrogen chloride produced. But the considerations regarding the byproducts still exist. The used of a combined process may also be helpful in the gradual change from reaction Scheme I to reaction Scheme II.

# BIBLIOGRAPHY

Aspen Technology, I. ASPEN PLUS User Guide. Cambridge: 1988.

"Chemical Profiles: Methyl Chloride." Chemical Marketing Report (March 9 1992).

"Chemical Prices." Chemical Marketing Reporter (Jan 2 1995): 27-30.

"Environmental Processes '93: Challenge in the 90's." Hydrocarbon Processing (August 1993): 71-72,105.

"Federal Register / Rules and Regulations." 19403-19454. 59. 1994.

"Montreal Protocol: Controlling Substances that Deplete the Ozone Layer." Department of State Bulletin 87 (2129 1987): 60-63.

Student Contest Problem 1964. American Institute of Chemical Engineers, 1964.

"Title 40, Part 261." In Code of Federal Regulations, Office of the Federal Register, 1994.

Waste Minimization Opportunity Assesment Manual. US Environmental Protection Agency, 1988. EPA/625/7-88/003.

Adriani, A., K. Arai, et al. "Operational Design of Chemical Plants Based on a Topological Approach." In AIChE Spring National Meeting in Houston, TX., 1995.

Akehata, T. "Pollution Prevention by Minimizing Waste Generation in a Chemical Production Process." Journal of Chemical Engineering of Japan 24 (3 1991): 273-283.

Becerra, A. M., A. E. L. Castro, et al. "Kinetics of the Catalytic Hydrochlorination of Methanol to Methyl Chloride." Industrial and Engineering Chemistry Research 31 (1992): 1040-1045.

Benforado, D. M. and G. Ridlehoover. "Pollution Prevention: One Firm's Experience." Chemical Engineering (September 1991): 130-133.

Buice, J. E., R. L. Bowlin, et al. "Hydrochloric Acid." In Encyclopedia of Chemical Processing and Design, ed. J. McKetta. 396-417. 26. New York: Dekker, 1987.

Carson, H. T. and D. B. Cox, eds. Handbook on Hazardous Materials Management. 4th ed., Institute of Hazardous Materials Management, 1992.

Chadha, N. "Develop Multimedia Pollution Prevention Strategies." Chemical Engineering Progress 90 (11 1994): 32-39.

Ciric, A. R. and C. A. Floudas. "A Mixed Integer Nonlinear Programming Model for Retrofitting Heat-Exchanger Networks." Industrial and Engineering Chemistry Research 29 (February (2) 1990): 239-251.

Cohen, Y. and D. Allen. "An Integrated Approach to Process Waste Minimization Research." Journal of Hazardous Materials 29 (1992): 237-253.

DeForest, E. M. "Chloromethanes." In Encyclopedia of Chemical Processing Design, ed. J. Mcketta. 214-270. 8. New York: Dekker, 1979.

Diwekar, U. "Personal Communication." 1994.

Diwekar, U. M. and E. S. Rubin. "Efficient Handling of the Implicit Constraints Problem for the ASPEN MINLP Synthesizer." Industrial & Engineering Chemistry Research 32 (9 1993): 2006-2011.

Diwekar, U. M., C. H. Frey, et al. "Synthesizing Optimal Flowsheets: Applications to IGCC System Environmental Control." Industrial and Engineering Chemistry Research 31 (August 1992a): 1927-1936.

Diwekar, U. M., I. E. Grossmann, et al. "An MINLP Process Synthesizer for a Sequential Modular Simulator." Industrial and Engineering Chemistry Research 31 (January 1992b): 313-322.

Dokurno, M. G. and P. L. Douglas. "Simulation of an Ethylene Oligomerization Reactor System Using ASPEN." The Canadian Journal of Chemical Engineering 62 (-- 1984): 818-824.

Douglas, J. M. Conceptual Design of Chemical Processes. McGraw-Hill Book Company, 1988.

Douglas, J. M. "Process Synthesis for Waste Minimization." Industrial and Engineering Chemistry Research 31 (January 1992): 238-243.

Douglas, J. M. and G. Stephanopoulos. "Heirarchical Approaches in Conceptual Process Design: Framework and Computer-Aided Implementation." In Foundations of Computer Aided Process Design '94 in Snowmass Village, Colorado, 1-15, 1994.

Douglas, J. M. and D. C. Woodcock. "Cost Diagrams and the Quick Screening of Process Alternatives." Industrial and Engineering Chemistry Research 24 (4 1987): 970-976.

Duran, M. A. and I. E. Grossmann. "An Outer-Approximation Algorithm for a Class of Mixed-Integer Nonlinear Programs." Mathematical Programming 36 (1986): 307-339.

Dyer, J. and K. Mulholland. "Toxic Air Emissions: What is the Full Cost to Your Business." Chemical Engineering 101 (February Supplement (2) 1994): 4-8.

Edgar, T.F. and D.M. Himmelblau. Optimization of Chemical Processes. McGraw-Hill Book Company, 1988.

El-Halwagi, M. M. and V. Manousiouthakis. "Synthesis of Mass Exchange Networks." AIChE Journal 35 (8 1989): 1233-1244.

Ellis, C. The Chemistry of Petroleum Derivatives. Vol. 1. New York: The Chemical Catalog Co., Inc., 1934.

Farag, I. H., C. C. Chen, et al. "Modeling Pollution Prevention." Chemtech 22 (January 1992): 54-61.

Farag, I., I. Gosling, et al. "Simulating Wastewater Treatment Processes." The Chemical Engineer (September 13 1990): 31-38.

Forlano, L. "Production of Methylene Chloride." Nov 12, 1974: 3,848,007, 1974.

Fouhy, K. "Process Simulation Gains a New Dimension." Chemical Engineering (October 1991): 47-52.

Freeman, H., T. Harten, et al. "Industrial Pollution Prevention: A Critical Review." Journal of Air and Waste Management Association 42 (May 1992): 619-653.

Gas Processors Suppliers Association, (GPSA). Engineering Data Book - Volume I. Revised 10th ed., Vol. I. ed. Gas Processors Association. Tulsa, OK, 1994.

Geoffrion, A. M. "Generalized Benders Decomposition." Journal of Optimization Theory and Applications 10 (4 1972): 237-260.

Glasscock, D. A. and J. C. Hale. "Process Simulation: The Art and Science of Modeling." Chemical Engineering 101 (November (11) 1994): 82-89.

Gossett, J. M. "Measurement of Henry's Law Constants for C1 and C2 Chlorinated Hydrocarbons." Environmental Science and Technology 21 (2 1987): 202-208.

Grinthal, W. "Process Simulators Shift Into High Gear." Chemical Engineering 100 (July 1993): 153-156.

Grossmann, I. E. "MINLP Optimization Strategies and Algorithms for Process Synthesis." In Third International Conference on Foundations of Computer-Aided Process Design in Snowmass Village, Colorado, edited by J. J. Siirola, I. E. Grossmann, and G. Stephanopoulos, Elseiver, 105-132, 1989.

Grossmann, I. E., W. A. Westerberg, et al. "Retrofit Design of Processes." In First International Conference on Foundations of Computer Aided Process Operations in Park City, Utah, edited by G.V. Reklaitis and H. D. Spriggs, Elseiver, 403-442, 1987.

Gundersen, T. "Retrofit Process Design Research and Applications of Systematic Methods." In Third International Conference on Foundations of Computer-Aided Process Design in Colorado, edited by Jeffrey J. Siirola, Ignacio E. Grossmann, and

Holbrook, M. T. "Methyl Chloride." In Kirk-Othmer Encyclopedia of Chemical Technology, ed. J. I. Kroschwitz. 1029-1040. 4th ed., Vol. 5. New York: John Wiley & Sons, 1993.

Holland, F. A., F. A. Watson, et al. Introduction to Process Economics. John Wiley & Sons, 1974.

Johnson, P. R., J. L. Parsons, et al. "Making Chloromethanes." Industrial and Engineering Chemistry 51 (April (4) 1959): 499-507.

Jordan, C. H. "Liquified Natural Gas: Natural Gas Processing at Low Temperatures." Chemical Engineering Progress 68 (9 1972): 52-55.

Karam, J. G., C. St. Cin, et al. "Economic Evaluation of Waste Minimization Options." Environmental Progress 7 (3 1988): 192-197.

Kocis, G. R. and I. E. Grossmann. "A Modeling and Decomposition Strategy for the MINLP Optimization of Process Flowsheets." Computers and Chemical Engineering 13 (7 1989): 797-819.

Kocis, G. R. and I. E. Grossmann. "Relaxation Strategy for the Structural Optimization of Process Flowsheets." Industrial & Engineering Chemistry Research 26 (1987): 1869-1880.

Kovalic, J. M. The Clean Water Act of 1987. Alexandria: Water Environment Federation, 1987.

Kuhre, W. L. Practical Management of Chemical and Hazardous Wastes. Englewood Cliffs: Prentice Hall, 1994.

LaGrega, M. D., P. L. Buckingham, et al. Hazardous Waste Management. New York: McGraw-Hill, 1994.

Linnhoff, B. "Use Pinch Analysis to Knock Down Capital Cost and Emissions." Chemical Engineering Progress 90 (August (8) 1994): 32-57.

Linnhoff, B., D. W. Townsend, et al. User Guide on Process Integration for the Efficient Use of Energy. ed. The Institution of Chemical Engineers. Greet Britain: Pergamon Press, 1982.

McBee, E. T., H. B. Hass, et al. "Chlorination of Methane." Industrial and Engineering Chemistry 34 (March (3) 1942): 296-300.

Mizsey, P. "Waste Reduction in the Chemical Industry: A Two Level Problem." Journal of Hazardous Materials 37 (1994): 1-13.

Morreto, H., S. Manfred, et al. "Silicones." In Ullmann's Encyclopedia of Industrial Chemistry, 57-93. A24. 1985.

Morris, J. W. and T. V. Robertson. "Modeling of a large multi-product industrial site to define wastewater minimization and treatment alternatives." In 66th Annual Conference & Exposition in Anaheim, California, edited by Water Environment Federation, , 294-304, 1993.

Oldershaw, C. F., L. Simenson, et al. "Absorption and Purification of Hydrogen Chloride from Chlorination of Hydrocarbons." Chemical Engineering Progress 43 (July (7) 1947): 371-378.

Papalexandri, K. P. and E. N. Pistikopoulos. "An MINLP Retrofit Approach for Improving the Flexibility of Heat Exchanger Networks." Annals of Operation Research 42 (1993): 119-168.

Perry, H. R. and D. Green. Perry's Chemical Engineers Handbook. 6th ed., McGraw-Hill Book Company, 1984.

Peters, M. S. and K. D. Timmerhaus. Plant Design and Economics for Chemical Engineers. 4th ed., New York: McGraw-Hill, 1991.

Petrides, D. P., K. G. Abeliotis, et al. "EnviroCAD: A Design Tool for Efficient Synthesis and Evaluation of Integrated Waste Recovery, Treatment and Disposal Processes." Computers and Chemical Engineering 18 (Supplement (ESCAPE - 3) 1994): S603-S607.

Polley, G. "Heat Exchanger Design and Process Integration." The Chemical Engineer - London (Apr 8 1993 (540) 1993): 16-18.

Quesada, I. and I. E. Grossmann. "An LP/NLP Based Branch and Bound Algorithm for Convex MINLP Optimization Problems." Computers in Chemical Engineering 16 (10/11 1992): 937-947.

Raman, R. and I. E. Grossmann. "Integration of Logic and Heuristic Knowledge in MINLP Optimization for Process Synthesis." Computers and Chemical Engineering 16 (3 1992): 155-171.

Raman, R. and I. E. Grossmann. "Symbolic Integration of Logic in Mixed-Integer Programming Techniques for Process Synthesis." Computers and Chemical Engineering 17 (9 1993): 909-927.

Rosain, R. M. "Reusing Water in CPI Plants." Chemical Engineering Progress 89 (April 1993): 28-35.

Schweitzer, P. A. Handbook of Separation Techniques for Chemical Engineers. 2nd ed., Mc Graw-Hill, 1988.

Turner, W. Hazardous Materials/Waste Management Certification Course in Waste Minimization. Oklahoma State University, 1994.

Scipioni, A. and E. Rapisardi. "Sul rapporto di formazione dei clorometani in funzione della cinetica di reazione." La Chimica e L'Industria 43 (November (11) 1961): 1286-1293.

Smith, J. M. Chemical Engineering Kinetics. 3rd ed., McGraw-Hill Chemical Engineering Series, New York: McGraw-Hill, 1981.

Thayer, A. M. "Pollution Reduction." Chemical and Engineering News 70 (46 1992): 22-52.

Thyagarajan, M. S., R. Kumar, et al. "Hydrochlorination of Methanol to Methyl Chloride in Fixed Catalyst Beds." I & EC Process Design and Development 5 (3 1966): 209-213.

Turner, W. Hazardous Materials/Waste Management Certification Course in Waste Minimization. Oklahoma State University,

Viswanathan, J. and I. E. Grossmann. A Combined Penalty Function and Outer-Approximation Method for MINLP Optimization - Applications to Distillation Column Design. Engineering Research Design Center, 1989. EDRC 06-74-89.

Weller, S. "Analysis of Kinetic Data for Heterogeneous Reactions." AIChE Journal 2 (1 1956): 59-62.

Woodman, H. J. "Why not Zero Waste?" EPA Journal (November/December 1989): 39-40.

Yee, T. F. and I. E. Grossmann. "Simultaneous Optimization Models for Heat Integration - II. Heat Exchanger Network Synthesis." Computers and Chemical Engineering 14 (10 1990): 1165-1184.

Yee, T. F., I. E. Grossmann, et al. "Simultaneous Optimization Models for Heat Integration - I. Area and Energy Targeting and Modeling of Multi-Stream Exchangers." Computers and Chemical Engineering 14 (10 1990a): 1151-1164.

Yee, T. F., I. E. Grossmann, et al. "Simultaneous Optimization Models for Heat Integration - III. Process and Heat Exchanger Network Optimization." Computers and Chemical Engineering 14 (11 1990b): 1185-1200.

Zanetti, R. "The Growing Cost of Cleanup." Chemical Engineering (May 1994): 5.

Zimmer, J. and R. Guaitella. "Incineration: Lowest Cost HCl Recovery." Hydrocarbon Processing 55 (August 1976): 117-118.

# APPENDIX A

# DETAILED MINLP ALGORITHM FOR CASE STUDY

### *Formulation of superstructure*

The base case and all the retrofit alternatives are used to formulate an overall flowsheet superstructure (see Figure 7.17). The objective function to be optimized is formulated using the economic model (see Equation A.1).

$$NPV = \sum_{j=1}^{ny} \left[ f_D \left( \Delta Mc(1 - Tx) + CF * D_f * Tx \right) \right] - CF \qquad (A.1)$$

The continuous variables $x$ were identified through the sensitivity analysis, and the discrete variables $y$ that represent the existence of a specified unit were identified through the hierarchical procedure. The discrete variables were defined using FSPLIT blocks by varying the flow fraction between 0 and 1.

Logic constraints are incorporated into the MINLP problem to reduce the number of alternatives to evaluate. To generate the logic constraints the superstructure is simplified by representing the splitters, mixers, input streams, and output streams as $Z$ blocks and the different processing unit sections by Y blocks (see Figure A.1), where:

Y1 = Initial unit operations for Scheme II
Y2 = Isothermal PFR for Scheme II
Y3 = Adiabatic PFR for Scheme II
Y4 = Separation sequence for Scheme II
Y5 = Initial unit operations for Scheme I
Y6 = Isothermal CSTR for Scheme I
Y7 = Isothermal PFR for Scheme I
Y8 = Initial separation sequence for Scheme I
Y9 = Separation sequence for base case
Y10 = Alternative base case separation sequence (common units)
Y11 = Alternative base case separation sequence with water
Y12 = Alternative base case separation sequence with no water
Z0 = Initial input stream to flowsheet
Z1 = Initial splitter to select between reaction Scheme I and II
Z2 = Splitter to select reactor system for Scheme II

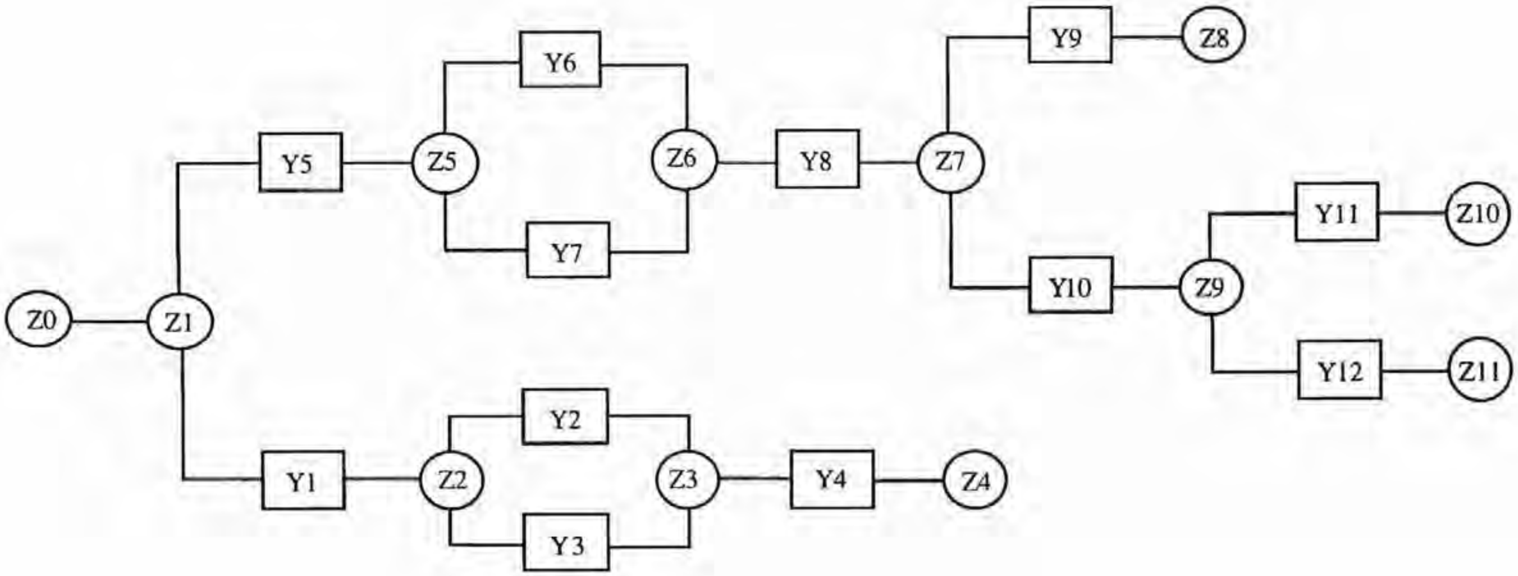

Figure A.1: Logic representation of superstructure

Z3 = Mixer

Z4 = Output stream for Scheme II

Z5 = Splitter to select reactor system for Scheme I

Z6 = Mixer

Z7 = Splitter to select between base case separation sequence and alternative separation sequences

Z8 = Output stream for base case

Z9 = Splitter to select between alternative base case separation sequence with or without water

Z10 = Output stream for alternative base case separation sequence with water

Z11 = Output stream for alternative base case separation sequence with no water

Based on figure A.1 we formulate a set of logic relationships (see Equation A.2)

$$
\begin{aligned}
&Z_0 \Leftrightarrow Z_1 \\
&Z_1 \Leftrightarrow Y_1 \vee Y_5 \\
&Y_1 \Leftrightarrow Z_2 \\
&Z_2 \Leftrightarrow Y_2 \vee Y_3 \\
&Y_2 \vee Y_3 \Leftrightarrow Z_3 \\
&Z_3 \Leftrightarrow Y_4 \\
&Y_4 \Leftrightarrow Z_4 \\
&Y_5 \Leftrightarrow Z_5 \\
&Z_5 \Leftrightarrow Y_6 \vee Y_7 \\
&Y_6 \vee Y_7 \Leftrightarrow Z_6 \\
&Z_6 \Leftrightarrow Y_8 \\
&Y_8 \Leftrightarrow Z_7 \\
&Z_7 \Leftrightarrow Y_9 \vee Y_{10} \\
&Y_9 \Leftrightarrow Z_8 \\
&Y_{10} \Leftrightarrow Z_9 \\
&Z_9 \Leftrightarrow Y_{11} \vee Y_{12} \\
&Y_{11} \Leftrightarrow Z_{10} \\
&Y_{12} \Leftrightarrow Z_{11}
\end{aligned} \qquad (A.2)
$$

Equation A.2 is analyzed and reduced in size. Since to have a product we need a feed to the flowsheet, then $Z_0$ has to be true. Therefore $Z_1$ and $Y_1 \vee Y_5$ have to be true. The first two equations in Equation A.2 can now be replaced by Equation A.3.

$$Y_1 \vee Y_5 \tag{A.3}$$

If $Y_1$ is true then $Z_2$ is true. Therefore, we can replace the next set of equations in Equation A.3 by Equation A.4.

$$Y_1 \Leftrightarrow Y_2 \vee Y_3 \tag{A.4}$$

If this procedure is followed until all $Z$ variables have been eliminated and Equation set A.2 has been reduced to its maximum, Equation A.5 is obtained.

$$\begin{aligned}
&Y_1 \vee Y_5\\
&Y_1 \Leftrightarrow Y_2 \vee Y_3\\
&Y_5 \Leftrightarrow Y_6 \vee Y_7\\
&Y_5 \Leftrightarrow Y_9 \vee Y_{10}\\
&Y_{10} \Leftrightarrow Y_{11} \vee Y_{12}
\end{aligned} \tag{A.5}$$

Equation A.5 is transformed, resulting in 13 constraints (see Equation A.6).

$$\begin{array}{lcl}
Y_1 \vee Y_5 & \rightarrow & Y_1 + Y_5 \geq 1\\
Y_1 \Leftrightarrow Y_2 \vee Y_3 & \rightarrow & Y_1 - Y_2 - Y_3 \leq 0\\
 & & Y_2 - Y_1 \leq 0\\
 & & Y_3 - Y_1 \leq 0\\
Y_5 \Leftrightarrow Y_6 \vee Y_7 & \rightarrow & Y_5 - Y_6 - Y_7 \leq 0\\
 & & Y_6 - Y_5 \leq 0\\
 & & Y_7 - Y_5 \leq 0\\
Y_5 \Leftrightarrow Y_9 \vee Y_{10} & \rightarrow & Y_5 - Y_9 - Y_{10} \leq 0\\
 & & Y_9 - Y_5 \leq 0\\
 & & Y_{10} - Y_5 \leq 0\\
Y_{10} \Leftrightarrow Y_{11} \vee Y_{12} & \rightarrow & Y_{10} - Y_{11} - Y_{12} \leq 0\\
 & & Y_{11} - Y_{10} \leq 0\\
 & & Y_{12} - Y_{10} \leq 0
\end{array} \tag{A.6}$$

An additional constraint is required to comply with the specified production demand (see Equation A.7).

$$f_{CH_3Cl-Y_8} + f_{CH_3Cl-Y_{10}} + f_{CH_3Cl-Y_{11}} + f_{CH_3Cl-Y_4} = 160 \qquad (A.7)$$

The final MINLP problem (see Equation A.1) consists of 9 continuous variables,

Scheme I

- Methane fresh feed rate
- Reaction temperature
- Reaction pressure
- Compressor outlet pressure
- Methyl chloride absorber pressure

Scheme II

- Hydrogen chloride fresh feed rate
- Reaction temperature
- Condenser outlet temperature
- Flash vessel pressure

10 discrete variables,

Scheme I

- Scheme I ($Y_5$)
- Isothermal CSTR ($Y_6$)
- Isothermal PFR ($Y_7$)
- Base case separation sequence ($Y_9$)
- Alternative separation sequence ($Y_{10}$)
- Alternative separation sequence with water ($Y_{11}$)
- Alternative separation sequence no water ($Y_{12}$)

Scheme II

- Scheme II ($Y_1$)
- Isothermal PFR ($Y_2$)
- Adiabatic PFR ($Y_3$)

, and 14 constraints.

### *MINLP Algorithm*

This section provides a step by step analysis of the MINLP algorithm applied to Section I of the superstructure. The same procedure is applied for the remaining sections.

Step 0: Initialization step

This step initializes all the variables required for the algorithm. The upper bound to the solution is set to infinity (see Equation A.8),

$$Z^u = \infty \qquad (A.8)$$

where:

$Z^u$ = upper bound to the solution

the list of open nodes that contains the nodes to be evaluated is initialized as an empty set (see Equation A.9),

$$P = \varnothing \qquad (A.9)$$

where:

$P$ = list of open nodes

The initial set of the integer variables $y^1$ that corresponds to the base case is fixed (see Equation A.10)

$$y^l = [\, Y_5, Y_6, Y_7, Y_9, Y_{10}, Y_{11}, Y_{12} \,] = [\, 1, 1, 0, 1, 0, 0, 0 \,] \qquad (A.10)$$

Step 1:

The integer variables $y^1$ is fixed by assigning the corresponding value in the FSPLIT block (see Equation A.11)

BLOCK *block id* FSPLIT
FRAC *outlet stream id* *frac* ( 0 or 1 ) (*A*.11)

The problem is now optimized using the ASPEN PLUS™ optimization block. The solution obtained (NPV=7.52 x $10^6$) provides an upper bound solution to the problem.

Step 2:

The integrality requirements of the set of discrete variables is relaxed and included as part of the optimization variables see Equation A.12.

```
VARY BLOCK-VAR BLOCK=block id SENTENCE=FRAC
      VARIABLE=FRAC ID1=outlet stream id                    (A.12)
LIMITS "0" "1"
```

The problem is optimized using the ASPEN PLUS™ optimization block. The results obtained provide a lower bound to the problem (NPV=7.52 x $10^6$) and the set containing the discrete variables results (see Equation A.13).

$$y^l = [\ Y_5, Y_6, Y_7, Y_9, Y_{10}, Y_{11}, Y_{12}\ ] = [\ 1, 1, 0, 1, 0, 0, 0\ ] \qquad (A.13)$$

For this case the list of open nodes remains empty (see Equation A.9). Since the solution provided is integer we go to step 6. The upper bound becomes 7.52 x $10^6$, and since the list of open nodes $P$ is empty this value corresponds to the optimal solution for the problem.

The algorithm, for Section I terminated due to the fact that an integer solution was found during the first iteration. This is convenient, but might not be always the case. To continue with the analysis of the algorithm, lets suppose the answer obtained in Step 2 is not integer (see Equation A.14).

$$y^l = [\ Y_5, Y_6, Y_7, Y_9, Y_{10}, Y_{11}, Y_{12}\ ] = [\ 1, 0.7, 0.3, 0.5, 0.5, 0, 0\ ] \quad (A.14)$$

Therefore, the list of open nodes, contains 4 elements (see Equation A.15)

$$P=[\ Y_6, Y_7, Y_9, Y_{10}\ ] \qquad (A.15)$$

In order to select the next variable to be branched in the solution tree (see Figure A.2), the list of feasible alternatives is generated (see Equation 6.7, A.16, and Figure A,1). Is important to remember that for Section I $Y_{12}$ is always zero and $Y_5$ is always one.

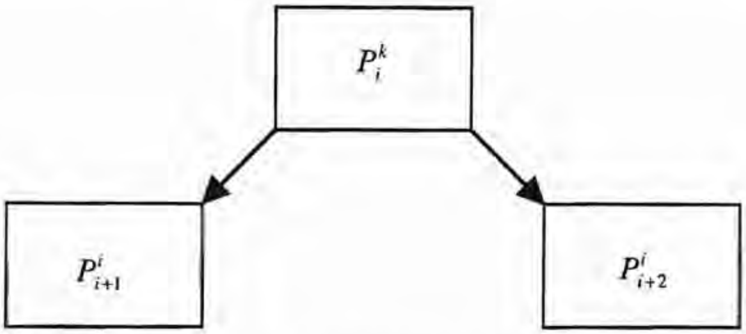

Figure A.2: Solution tree

$$\begin{aligned}\Omega_D = &(Y_5 \wedge Y_6 \wedge \neg Y_7 \wedge Y_8 \wedge Y_9 \wedge \neg Y_{10} \wedge \neg Y_{11} \wedge \neg Y_{12}) \vee \\ &(Y_5 \wedge Y_6 \wedge \neg Y_7 \wedge Y_8 \wedge \neg Y_9 \wedge Y_{10} \wedge Y_{11} \wedge \neg Y_{12}) \vee \qquad (A.16) \\ &(Y_5 \wedge \neg Y_6 \wedge Y_7 \wedge Y_8 \wedge \neg Y_9 \wedge Y_{10} \wedge Y_{11} \wedge \neg Y_{12}) \vee \\ &(Y_5 \wedge \neg Y_6 \wedge Y_7 \wedge Y_8 \wedge Y_9 \wedge \neg Y_{10} \wedge \neg Y_{11} \wedge \neg Y_{12})\end{aligned}$$

The next variable to be branched is selected based on the number of appearances of each variable in Equation A.16 (see Equation 6.6). The number of occurrences of $Y_i$ ($Y_i$ = 1) is represented by $\alpha_i$, and the number of occurrences of $\neg Y_i$ ($Y_i = 0$) is represented by $\beta_i$. Based on Equation 6.6 we obtain:

$$\begin{aligned} \alpha_6 &= 2 & \beta_6 &= 2 \\ \alpha_7 &= 2 & \beta_7 &= 2 \\ \alpha_9 &= 2 & \beta_9 &= 2 \\ \alpha_{10} &= 2 & \beta_{10} &= 2 \\ \alpha_{11} &= 2 & \beta_{11} &= 2 \end{aligned}$$

Based on Equation 6.6, the next variable to be branched is identified by having the minimum $\alpha_i$, and $\beta_i$. Since this criteria is not helpful for this case, the next criteria used is to select the variable with the closest value to 0.5. For this case we could choose $Y_9$ or $Y_{10}$ (see Equation A.14). Lets select $Y_9$.

The next step consists in applying the logical chaining approach that attempts to fix as many other binary variables as possible, by analyzing the logic representation of the superstructure (see Equation 6.8). If $Y_9$ is set to 0, then based on Equation A.16 $Y_{10}$ and $Y_{11}$ have to be equal to 1. If $Y_9$ is set to 1, then based on Equation A.16 $Y_{10}$ and $Y_{11}$ have to be equal to 0.

The next variable to be branched and other variables to be fixed are used to define two new problems in the solution tree (see Figure A.3).

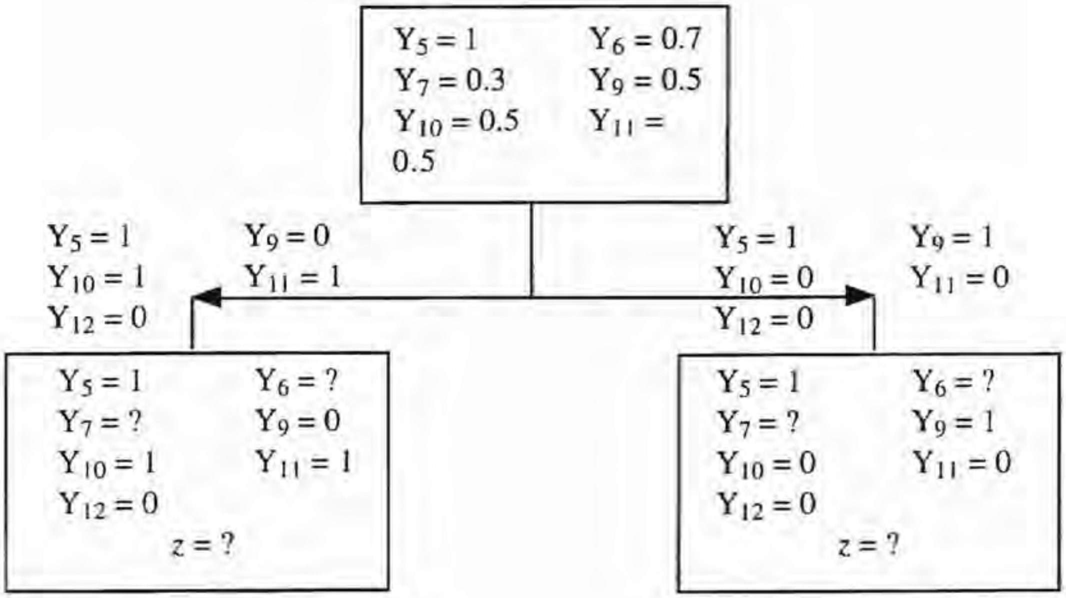

Figure A.3: Modified Solution Tree

Based on the solution tree a set of constraints is added for each new branch (see Equation A.17 and A.18). Equation A.17 represents the case for $Y_9 = 0$ and Equation A.18 represents the case for $Y_9 = 1$.

$$Y_9 \leq 0 \qquad Y_{10} \geq 1 \qquad Y_{11} \geq 1 \tag{A.17}$$

$$Y_9 \geq 1 \qquad Y_{10} \leq 0 \qquad Y_{11} \leq 0 \tag{A.18}$$

Step 4:

Each of the nodes in the solution tree is evaluated using the ASPEN PLUS™ optimization block. The solution is compared against the upper bound. Based on this comparison, the node can be eliminated from the list of nodes. If the solution is integer we go again to step 6.

Step 5:

The last two steps are repeated, until all nodes have been evaluated. If the list of open nodes is empty go to step 8.

Step 6: If the solution obtained is less than the upper bound, then the NLP solution becomes the new upper bound.

Step 7: Delete all nodes from the list of open nodes, for which their objective function value is greater or equal than the upper bound. Return to step 4.

Step 8: The current upper bound corresponds to the optimal solution for the MINLP problem.

# APPENDIX B
# INPUT FILE FOR BASE CASE PROCESS

```
TITLE 'Methyl Chloride Production - Base Case'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=1000

DATABANKS AQUEOUS / ASPENPCD / PURECOMP / SOLIDS / &
    INORGANIC

PROP-SOURCES AQUEOUS / ASPENPCD / PURECOMP / SOLIDS / &
    INORGANIC

COMPONENTS
  H2O H2O H2O /
  HCL HCL HCL /
  H+ H+ H+ /
  CL- CL- CL- /
  CL2 CL2 CL2 /
  CH4 CH4 CH4 /
  CH3CL CH3CL CH3CL /
  CH2CL2 CH2CL2 CH2CL2 /
  CHCL3 CHCL3 CHCL3 /
  CCL4 CCL4 CCL4

HENRY-COMPS ALL HCL CH4 CH3CL CH2CL2 CHCL3 CCL4 CL2

CHEMISTRY HCL
  STOIC 1 HCL -1.0 / H+ 1.0 / CL- 1.0

FLOWSHEET
  BLOCK B1 IN=18 REAC1 OUT=1
  BLOCK B2 IN=1 OUT=2
  BLOCK B5 IN=7 OUT=12
  BLOCK B6 IN=H2O-1 12 OUT=13 W1
  BLOCK B7 IN=13 OUT=14 W2
  BLOCK B8 IN=14 OUT=15
  BLOCK B9 IN=15 OUT=16
```

```
   BLOCK B10 IN=16 OUT=17 20
   BLOCK B11 IN=17 OUT=18
   BLOCK B12 IN=20 OUT=CH3CL 21
   BLOCK B14 IN=21 OUT=CH2CL2 23
   BLOCK B16 IN=23 OUT=CHCL3 W4
   BLOCK B32 IN=2 OUT=7

PROPERTIES ELECNRTL HENRY-COMPS=ALL CHEMISTRY=HCL TRUE-
COMPS=NO

PROP-DATA HENRY-1
   IN-UNITS SI
   PROP-LIST HENRY
   BPVAL HCL H2O 58.452960 -7762.8320 .0 .0 .0 1000.0
   BPVAL CL2 H2O 169.5452 -9487.196 -20.81234 0.0 273.0000  &
     400.0000
   BPVAL CH4 H2O 195.2940 -9111.670 -25.03790 1.43434E-4  &
     275.0000 353.0000
   BPVAL CH3CL H2O 184.0280 -9768.620 -23.42400 0.0 277.0000  &
     353.0000
   BPVAL HCL CH2CL2 98.21400 -4274.800 -12.77600 .0142190  &
     223.1500 273.1500
   BPVAL HCL CHCL3 -70.24690 -616.8900 18.38500 -.0574480  &
     223.1500 288.1500
   BPVAL HCL CH3OH -36.00520 1643.800 7.527300 0.0 275.2500  &
     307.3500
   BPVAL CL2 CCL4 -63.31090 -37.09400 14.68000 -.0227680  &
     253.1500 344.1500
   BPVAL CH4 CCL4 40.76590 -1168.800 -3.554400 2.66100E-3  &
     253.3500 333.1500
   BPVAL CH4 CH3OH -62.11760 1140.200 15.18900 -.0323600  &
     263.1500 303.1500
   BPVAL CH2CL2 H2O 29.1040 -3817.0 .0 .0 283.0 308.0
   BPVAL CHCL3 H2O 32.2940 -4612.0 .0 .0 283.0 308.0
   BPVAL CCL4 H2O 33.7410 -4411.0 .0 .0 283.0 308.0
   BPVAL CH3OH H2O 124.841 .0 21.43 .0 338.0 637.0

PROP-DATA GMELCC-1
   IN-UNITS SI
```

```
  PROP-LIST GMELCC
  PPVAL H2O ( H+ CL- ) 41.6740
  PPVAL ( H+ CL- ) H2O -22.1540
  PPVAL HCL ( H+ CL- ) .0010
  PPVAL ( H+ CL- ) HCL -.0010

PROP-DATA GMELCD-1
  IN-UNITS SI
  PROP-LIST GMELCD
  PPVAL H2O ( H+ CL- ) 5323.10
  PPVAL ( H+ CL- ) H2O -2204.10

PROP-DATA GMELCE-1
  IN-UNITS SI
  PROP-LIST GMELCE
  PPVAL H2O ( H+ CL- ) -5.4040
  PPVAL ( H+ CL- ) H2O 5.1880

PROP-DATA GMELCN-1
  IN-UNITS SI
  PROP-LIST GMELCN
  PPVAL H2O ( H+ CL- ) .028350
  PPVAL ( H+ CL- ) H2O .028350

STREAM REAC1
  SUBSTREAM MIXED TEMP=77 PRES=14.7
  MOLE-FLOW CL2 330 / CH4 280

STREAM H2O-1
  SUBSTREAM MIXED TEMP=90 PRES=14.7
  MOLE-FLOW H2O 0.001

BLOCK B1 MIXER

BLOCK B7 SEP
  FRAC STREAM=W2 SUBSTREAM=MIXED COMPS=H2O HCL H+ CL- CL2  &
    CH4 CH3CL CH2CL2 CHCL3 CCL4 CH3OH FRACS=1 1 0 0 0  &
    0 0 0 0 0 0
```

```
BLOCK B6 SEP
  FRAC STREAM=13 SUBSTREAM=MIXED COMPS=H2O HCL H+ CL-  &
    CL2 CH4 CH3CL CH2CL2 CHCL3 CCL4 CH3OH FRACS=0.249 0.001 &
    1 1 1 1 1 1 1 1 1

BLOCK B2 HEATER
  PARAM TEMP=572 PRES=0

BLOCK B5 HEATER
  PARAM TEMP=77 PRES=0

BLOCK B9 HEATER
  PARAM TEMP=-58 PRES=0

BLOCK B10 FLASH2
  PARAM PRES=0 DUTY=0

BLOCK B12 RADFRAC
  PARAM NSTAGE=10
  FEEDS 20 5
  PRODUCTS CH3CL 1 V / 21 10 L
  P-SPEC 1 14.7
  COL-SPECS D:F=0.9 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=1.2
  SPEC 1 MOLE-RECOV 0.99 COMPS=CH3CL STREAMS=CH3CL
  VARY 1 D:F 0.001 0.999

BLOCK B14 RADFRAC
  PARAM NSTAGE=40
  FEEDS 21 20 ON-STAGE
  PRODUCTS CH2CL2 1 V / 23 40 L
  P-SPEC 1 14.7
  COL-SPECS D:F=0.5 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=1.3
  SPEC 1 MOLE-RECOV 0.99 COMPS=CH2CL2 STREAMS=CH2CL2
  VARY 1 D:F 0.001 0.999

BLOCK B16 DSTWU
  PARAM LIGHTKEY=CHCL3 RECOVL=0.999 HEAVYKEY=CCL4  &
    RECOVH=0.001 PTOP=15 PBOT=15 NSTAGE=10
```

```
BLOCK B32 RCSTR
  PARAM VOL=1600 TEMP=902 PRES=0
  REACTIONS RXN-IDS=RSCH-1

BLOCK B8 COMPR
  PARAM TYPE=RIG-POLYTROP PRES=115 TEMP=275

BLOCK B11 COMPR
  PARAM TYPE=RIG-POLYTROP DELP=30

DESIGN-SPEC FEED
  DEFINE FCH4 MOLE-FLOW STREAM=2 SUBSTREAM=MIXED &
    COMPONENT=CH4
  DEFINE FCL2 MOLE-FLOW STREAM=2 SUBSTREAM=MIXED &
    COMPONENT=CL2
F   RATIO=FCL2/FCH4
  SPEC "RATIO" TO "0.3"
  TOL-SPEC "0.01"
  VARY MOLE-FLOW STREAM=REAC1 SUBSTREAM=MIXED
COMPONENT=CH4
  LIMITS "200" "1000"

DESIGN-SPEC PROD
  DEFINE FCH3CL MOLE-FLOW STREAM=CH3CL SUBSTREAM=MIXED &
    COMPONENT=CH3CL
  SPEC "FCH3CL" TO "160"
  TOL-SPEC "1"
  VARY MOLE-FLOW STREAM=REAC1 SUBSTREAM=MIXED
COMPONENT=CL2
  LIMITS "300" "500"

DESIGN-SPEC H2O1
  DEFINE MHCL MOLE-FLOW STREAM=12 SUBSTREAM=MIXED &
    COMPONENT=HCL
  DEFINE MH2O1 MOLE-FLOW STREAM=H2O-1 SUBSTREAM=MIXED &
    COMPONENT=H2O
F   WATER=4.855*MHCL-6.143
F   C21=WATER-MH2O1
  SPEC "C21" TO "0"
```

```
   TOL-SPEC "0.1"
   VARY MOLE-FLOW STREAM=H2O-1 SUBSTREAM=MIXED COMPONENT=H2O
   LIMITS "0" "5000"

REACTIONS RSCH-1 POWERLAW
   REAC-DATA 1 PHASE=V CBASIS=MOLARITY
   REAC-DATA 2 PHASE=V CBASIS=MOLARITY
   REAC-DATA 3 PHASE=V CBASIS=MOLARITY
   REAC-DATA 4 PHASE=V CBASIS=MOLARITY
   RATE-CON 1 PRE-EXP=2.56E8 ACT-ENERGY=35260
   RATE-CON 2 PRE-EXP=6.28E7 ACT-ENERGY=30580
   RATE-CON 3 PRE-EXP=2.56E8 ACT-ENERGY=35260
   RATE-CON 4 PRE-EXP=2.93E8 ACT-ENERGY=37490
   STOIC 1 MIXED CH4 -1 / CL2 -1 / CH3CL 1 / HCL 1
   STOIC 2 MIXED CH3CL -1 / CL2 -1 / CH2CL2 1 / HCL 1
   STOIC 3 MIXED CH2CL2 -1 / CL2 -1 / CHCL3 1 / HCL 1
   STOIC 4 MIXED CHCL3 -1 / CL2 -1 / CCL4 1 / HCL 1
   POWLAW-EXP 1 MIXED CH4 1 / MIXED CL2 1
   POWLAW-EXP 2 MIXED CH3CL 1 / MIXED CL2 1
   POWLAW-EXP 3 MIXED CH2CL2 1 / MIXED CL2 1
   POWLAW-EXP 4 MIXED CHCL3 1 / MIXED CL2 1
```

# APPENDIX C

# INPUT FILE FOR HYDROCHLORINATION OF METHANOL

```
TITLE 'Methyl Chloride Production - Hydrochlorination of Methanol'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=15000 MAX-ERRORS=1000000  &
  MAX-FORT-ERRORS=100000

DATABANKS AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  /  &
    INORGANIC

PROP-SOURCES AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  /  &
    INORGANIC

COMPONENTS
  H2O H2O H2O /
  HCL HCL HCL /
  CH3CL CH3CL CH3CL /
  CH3OH CH4O CH3OH

FLOWSHEET
  BLOCK B17 IN=REAC2 60 OUT=50
  BLOCK B25 IN=50 OUT=51
  BLOCK B27 IN=59 OUT=53
  BLOCK B28 IN=53 OUT=54 55
  BLOCK B29 IN=54 OUT=CH3CL-B W5
  BLOCK B33 IN=55 OUT=56 W6
  BLOCK B38 IN=51 OUT=59
  BLOCK B42 IN=56 OUT=60

PROPERTIES NRTL-RK

STREAM REAC2
  SUBSTREAM MIXED TEMP=77 PRES=14.7
  MOLE-FLOW HCL 194 / CH3OH 180

BLOCK B17 MIXER
```

```
BLOCK B29 SEP
  FRAC STREAM=CH3CL-B SUBSTREAM=MIXED COMPS=H2O HCL  &
    CH3CL CH3OH FRACS=0 0  &
    0.999 0

BLOCK B33 SEP
  FRAC STREAM=56 SUBSTREAM=MIXED COMPS=H2O HCL  &
    CH3CL CH3OH FRACS=0 0.95  &
    0 0

BLOCK B25 HEATER
  PARAM TEMP=662 PRES=0

BLOCK B27 HEATER
  PARAM TEMP=90 PRES=0

BLOCK B28 FLASH2
  PARAM PRES=0 DUTY=0

BLOCK B38 RPLUG
  PARAM TYPE=T-SPEC LENGTH=12 DIAM=10
  REACTIONS RXN-IDS=RSCH-2

BLOCK B42 COMPR
  PARAM TYPE=RIG-POLYTROP DELP=30

REACTIONS RSCH-2 POWERLAW
  REAC-DATA 1 PHASE=V CBASIS=MOLARITY
  RATE-CON 1 PRE-EXP=2.52E10 ACT-ENERGY=38700
  STOIC 1 MIXED CH3OH -1 / HCL -1 / CH3CL 1 / H2O 1
  POWLAW-EXP 1 MIXED CH3OH 1 / MIXED HCL 1
```

# APPENDIX D
# INPUT FILE FOR SECTION I

```
TITLE 'Methyl Chloride Production - Section I'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=15000 MAX-ERRORS=1000000  &
  MAX-FORT-ERRORS=100000

DATABANKS AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  /  &
    INORGANIC

PROP-SOURCES AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  /  &
    INORGANIC

COMPONENTS
  H2O H2O H2O /
  HCL HCL HCL /
  CL2 CL2 CL2 /
  CH4 CH4 CH4 /
  CH3CL CH3CL CH3CL /
  CH2CL2 CH2CL2 CH2CL2 /
  CHCL3 CHCL3 CHCL3 /
  CCL4 CCL4 CCL4

FLOWSHEET
  BLOCK B1 IN=18 39 REAC1 OUT=1
  BLOCK B2 IN=1 OUT=2
  BLOCK B3 IN=2 OUT=3 5
  BLOCK B4 IN=7 9 OUT=11 25
  BLOCK B5 IN=11 OUT=12
  BLOCK B6 IN=H2O-1 12 OUT=13 W1
  BLOCK B7 IN=13 OUT=14 W2
  BLOCK B8 IN=14 OUT=15
  BLOCK B9 IN=15 OUT=16
  BLOCK B10 IN=16 OUT=17 20
  BLOCK B11 IN=17 OUT=18
  BLOCK B12 IN=20 OUT=CH3CL 21
  BLOCK B13 IN=5 OUT=6
  BLOCK B14 IN=21 OUT=CH2CL2 23
  BLOCK B16 IN=23 OUT=CHCL3 W4
  BLOCK B18 IN=96 OUT=101 28
  BLOCK B19 IN=101 OUT=27
  BLOCK B20 IN=H2O-2 27 OUT=19 W3
  BLOCK B30 IN=41 OUT=26
  BLOCK B31 IN=26 OUT=100
  BLOCK B32 IN=3 OUT=7
  BLOCK B35 IN=6 OUT=9
  BLOCK B36 IN=19 OUT=42 W7
  BLOCK B37 IN=25 OUT=41
  BLOCK B40 IN=42 OUT=39
```

```
  BLOCK B47 IN=100 OUT=96 89 92
  BLOCK B51 IN=28 OUT=HCL1 97
  BLOCK B55 IN=97 OUT=CH3CL-E 98
  BLOCK B56 IN=98 OUT=CH2D 99
  BLOCK B57 IN=99 OUT=CHD W10

PROPERTIES NRTL-RK

STREAM REAC1
  SUBSTREAM MIXED TEMP=77 PRES=14.7
  MOLE-FLOW CL2 331 / CH4 280

STREAM H2O-1
  SUBSTREAM MIXED TEMP=90 PRES=14.7
  MOLE-FLOW H2O 0.001

STREAM H2O-2
  SUBSTREAM MIXED TEMP=90 PRES=14.7
  MOLE-FLOW H2O 0.001

BLOCK B1 MIXER

BLOCK B3 FSPLIT
  FRAC 3 1

BLOCK B4 FSPLIT
  FRAC 11 1

BLOCK B47 FSPLIT
  FRAC 96 1 / 89 0

BLOCK B6 SEP
  FRAC STREAM=13 SUBSTREAM=MIXED COMPS=H2O HCL  &
     CL2 CH4 CH3CL CH2CL2 CHCL3 CCL4 FRACS=0.249 0.001 &
     1 1 1 1 1 1
  FLASH-SPECS 13 PRES=14.7 TEMP=158 NPHASE=1 PHASE=V
  FLASH-SPECS W1 PRES=14.7 TEMP=90 NPHASE=1 PHASE=L

BLOCK B7 SEP
  FRAC STREAM=W2 SUBSTREAM=MIXED COMPS=H2O HCL CL2  &
    CH4 CH3CL CH2CL2 CHCL3 CCL4 FRACS=1 1 0   &
     0 0 0 0 0

BLOCK B20 SEP
  FRAC STREAM=19 SUBSTREAM=MIXED COMPS=H2O HCL  &
     CL2 CH4 CH3CL CH2CL2 CHCL3 CCL4 FRACS=0.249 0.001 &
     1 1 1 1 1 1
  FLASH-SPECS 19 PRES=14.7 TEMP=158 NPHASE=1 PHASE=V
  FLASH-SPECS W3 PRES=14.7 TEMP=90 NPHASE=1 PHASE=L
```

```
BLOCK B36 SEP
  FRAC STREAM=W7 SUBSTREAM=MIXED COMPS=H2O HCL CL2 &
    CH4 CH3CL CH2CL2 CHCL3 CCL4 FRACS=1 1 0 &
    0 0 0 0 0

BLOCK B2 HEATER
  PARAM TEMP=572 PRES=0

BLOCK B5 HEATER
  PARAM TEMP=77 PRES=0

BLOCK B9 HEATER
  PARAM TEMP=-58 PRES=0

BLOCK B13 HEATER
  PARAM TEMP=842 PRES=0

BLOCK B19 HEATER
  PARAM TEMP=77 PRES=14.7

BLOCK B31 HEATER
  PARAM TEMP=-58 PRES=0

BLOCK B37 HEATER
  PARAM TEMP=-58 PRES=0

BLOCK B10 FLASH2
  PARAM PRES=0 DUTY=0

BLOCK B18 FLASH2
  PARAM PRES=0 DUTY=0

BLOCK B12 RADFRAC
  PARAM NSTAGE=10
  FEEDS 20 5
  PRODUCTS CH3CL 1 V / 21 10 L
  P-SPEC 1 14.7
  COL-SPECS D:F=0.9 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=1.2
  SPEC 1 MOLE-RECOV 0.99 COMPS=CH3CL STREAMS=CH3CL
  VARY 1 D:F 0.001 0.999

BLOCK B14 RADFRAC
  PARAM NSTAGE=40
  FEEDS 21 20 ON-STAGE
  PRODUCTS CH2CL2 1 V / 23 40 L
  P-SPEC 1 14.7
  COL-SPECS D:F=0.5 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=1.3
  SPEC 1 MOLE-RECOV 0.99 COMPS=CH2CL2 STREAMS=CH2CL2
  VARY 1 D:F 0.001 0.999
```

```
BLOCK B51 RADFRAC
  PARAM NSTAGE=10
  FEEDS 28 5
  PRODUCTS 97 10 L / HCL1 1 V
  P-SPEC 1 14.7
  COL-SPECS D:F=0.55 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=0.25
  SPEC 1 MOLE-RECOV 0.99 COMPS=HCL STREAMS=HCL1
  VARY 1 D:F 0.001 0.999
  SIZE-DATA COND=YES REB=YES

BLOCK B55 RADFRAC
  PARAM NSTAGE=10
  FEEDS 97 5 ON-STAGE
  PRODUCTS 98 10 L / CH3CL-E 1 V
  P-SPEC 1 14.7
  COL-SPECS D:F=0.9 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=1.2
  SPEC 1 MOLE-RECOV 0.99 COMPS=CH3CL STREAMS=CH3CL-E
  VARY 1 D:F 0.001 0.999
  SIZE-DATA COND=YES REB=YES

BLOCK B56 RADFRAC
  PARAM NSTAGE=40
  FEEDS 98 20 ON-STAGE
  PRODUCTS 99 40 L / CH2D 1 V
  P-SPEC 1 14.7
  COL-SPECS D:F=0.5 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=1.3
  SPEC 1 MOLE-RECOV 0.99 COMPS=CH2CL2 STREAMS=CH2D
  VARY 1 D:F 0.001 0.999
  SIZE-DATA COND=YES REB=YES

BLOCK B16 DSTWU
  PARAM LIGHTKEY=CHCL3 RECOVL=0.999 HEAVYKEY=CCL4  &
     RECOVH=0.001 PTOP=15 PBOT=15 NSTAGE=10

BLOCK B57 DSTWU
  PARAM LIGHTKEY=CHCL3 RECOVL=0.999 HEAVYKEY=CCL4  &
     RECOVH=0.001 PTOP=15 PBOT=15 NSTAGE=10

BLOCK B32 RCSTR
  PARAM VOL=1600 TEMP=842 PRES=0
  REACTIONS RXN-IDS=RSCH-1

BLOCK B35 RPLUG
  PARAM TYPE=T-SPEC LENGTH=60 DIAM=3
  REACTIONS RXN-IDS=RSCH-1

BLOCK B8 COMPR
  PARAM TYPE=RIG-POLYTROP PRES=115 TEMP=275

BLOCK B11 COMPR
  PARAM TYPE=RIG-POLYTROP DELP=30
```

```
BLOCK B30 COMPR
  PARAM TYPE=POLYTROPIC PRES=115

BLOCK B40 COMPR
  PARAM TYPE=RIG-POLYTROP DELP=30

PROJECT-DATE
  START MONTH=JANUARY YEAR=1995
  PURCHASE MONTH=JANUARY YEAR=1995

COST-INDEX
  EQUIPMENT

CBLOCK E-2 H-VESSEL
  SIZING-DATA VOL=1600
  REFERENCE BLOCK=B35

CBLOCK E-4 V-VESSEL
  SIZING-DATA VOL=500
  REFERENCE BLOCK=B18

CBLOCK E-10 COMPR
  REFERENCE BLOCK=B30

CBLOCK E-12 COMPR
  REFERENCE BLOCK=B40

CBLOCK E-21 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B51

CBLOCK E-22 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B55

CBLOCK E-23 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B56

CBLOCK E-24 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B57

FORTRAN INIT
  DEFINE POWB8 BLOCK-VAR BLOCK=B8 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
  DEFINE POWB11 BLOCK-VAR BLOCK=B11 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
  DEFINE QCB12 BLOCK-VAR BLOCK=B12 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
```

```
   DEFINE QHB12 BLOCK-VAR BLOCK=B12 VARIABLE=REB-DUTY &
     SENTENCE=RESULTS
   DEFINE QCB14 BLOCK-VAR BLOCK=B14 VARIABLE=COND-DUTY &
     SENTENCE=RESULTS
   DEFINE QHB14 BLOCK-VAR BLOCK=B14 VARIABLE=REB-DUTY &
     SENTENCE=RESULTS
   DEFINE QCB16 BLOCK-VAR BLOCK=B16 VARIABLE=COND-DUTY &
     SENTENCE=RESULTS
   DEFINE QHB16 BLOCK-VAR BLOCK=B16 VARIABLE=REB-DUTY &
     SENTENCE=RESULTS
   DEFINE POWB30 BLOCK-VAR BLOCK=B30 VARIABLE=IND-POWER &
     SENTENCE=RESULTS
   DEFINE QCB32 BLOCK-VAR BLOCK=B32 VARIABLE=QCALC &
     SENTENCE=PARAM
   DEFINE QCB35 BLOCK-VAR BLOCK=B35 VARIABLE=QCALC &
     SENTENCE=PARAM
   DEFINE POWB40 BLOCK-VAR BLOCK=B40 VARIABLE=IND-POWER &
     SENTENCE=RESULTS
   DEFINE QCB51 BLOCK-VAR BLOCK=B51 VARIABLE=COND-DUTY &
     SENTENCE=RESULTS
   DEFINE QHB51 BLOCK-VAR BLOCK=B51 VARIABLE=REB-DUTY &
     SENTENCE=RESULTS
   DEFINE QCB55 BLOCK-VAR BLOCK=B55 VARIABLE=COND-DUTY &
     SENTENCE=RESULTS
   DEFINE QHB55 BLOCK-VAR BLOCK=B55 VARIABLE=REB-DUTY &
     SENTENCE=RESULTS
   DEFINE QCB56 BLOCK-VAR BLOCK=B56 VARIABLE=COND-DUTY &
     SENTENCE=RESULTS
   DEFINE QHB56 BLOCK-VAR BLOCK=B56 VARIABLE=REB-DUTY &
     SENTENCE=RESULTS
   DEFINE QCB57 BLOCK-VAR BLOCK=B57 VARIABLE=COND-DUTY &
     SENTENCE=RESULTS
   DEFINE QHB57 BLOCK-VAR BLOCK=B57 VARIABLE=REB-DUTY &
     SENTENCE=RESULTS
   DEFINE CSTB18 CBLOCK-VAR CBLOCK= E-4 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
   DEFINE CSTB30 CBLOCK-VAR CBLOCK= E-10 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
   DEFINE CSTB35 CBLOCK-VAR CBLOCK= E-2 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
   DEFINE CSTB40 CBLOCK-VAR CBLOCK= E-12 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
   DEFINE CSTB51 CBLOCK-VAR CBLOCK= E-21 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
   DEFINE CSTB55 CBLOCK-VAR CBLOCK= E-22 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
   DEFINE CSTB56 CBLOCK-VAR CBLOCK= E-23 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
   DEFINE CSTB57 CBLOCK-VAR CBLOCK= E-24 VARIABLE=TOT-COST &
     SENTENCE=RESULTS
F     POWB8=0
```

```
F    POWB11=0
F    QCB12=0
F    QHB12=0
F    QCB14=0
F    QHB14=0
F    QCB16=0
F    QHB16=0
F    POWB30=0
F    QCB32=0
F    QCB35=0
F    POWB40=0
F    QCB51=0
F    QHB51=0
F    QCB55=0
F    QHB55=0
F    QCB56=0
F    QHB56=0
F    QCB57=0
F    QHB57=0
F    CSTB18=0
F    CSTB30=0
F    CSTB35=0
F    CSTB40=0
F    CSTB55=0
F    CSTB56=0
F    CSTB57=0
  EXECUTE FIRST

DESIGN-SPEC H2O1
  DEFINE MHCL MOLE-FLOW STREAM=12 SUBSTREAM=MIXED &
    COMPONENT=HCL
  DEFINE MH2O1 MOLE-FLOW STREAM=H2O-1 SUBSTREAM=MIXED &
    COMPONENT=H2O
F    WATER=4.855*MHCL-6.143
F    C21=WATER-MH2O1
  SPEC "C21" TO "0"
  TOL-SPEC "0.1"
  VARY MOLE-FLOW STREAM=H2O-1 SUBSTREAM=MIXED COMPONENT=H2O
  LIMITS "0" "5000"

DESIGN-SPEC H2O2
  DEFINE MHCL MOLE-FLOW STREAM=27 SUBSTREAM=MIXED &
    COMPONENT=HCL
  DEFINE MH2O2 MOLE-FLOW STREAM=H2O-2 SUBSTREAM=MIXED &
    COMPONENT=H2O
  DEFINE FR11 BLOCK-VAR BLOCK=B4 SENTENCE=FRAC &
    VARIABLE=FRAC ID1=11
F    FR25=1-FR11
F    WATER=(4.855*MHCL-6.143)*FR25
F    C22=WATER-MH2O2
  SPEC "C22" TO "0"
```

```
  SPEC "C22" TO "0"
  TOL-SPEC "0.1"
  VARY MOLE-FLOW STREAM=H2O-2 SUBSTREAM=MIXED COMPONENT=H2O
  LIMITS "0" "5000"

CONSTRAINT C-1
  DEFINE MCH3 MOLE-FLOW STREAM=CH3CL SUBSTREAM=MIXED  &
    COMPONENT=CH3CL
  DEFINE MCH3E MOLE-FLOW STREAM=CH3CL-E SUBSTREAM=MIXED  &
    COMPONENT=CH3CL
F    PROD=MCH3+MCH3E
  SPEC "PROD" EQ "160"
  TOL-SPEC "0.1"

OPTIMIZATION O-1
  DEFINE MCH3 MASS-FLOW STREAM=CH3CL SUBSTREAM=MIXED  &
    COMPONENT=CH3CL
  DEFINE MCH3E MASS-FLOW STREAM=CH3CL-E SUBSTREAM=MIXED  &
    COMPONENT=CH3CL
  DEFINE HCL1 MASS-FLOW STREAM=HCL1 SUBSTREAM=MIXED  &
    COMPONENT=HCL
  DEFINE VCH2 STREAM-VAR STREAM=CH2CL2 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VCH2D STREAM-VAR STREAM=CH2D SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VCHCL3 STREAM-VAR STREAM=CHCL3 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VCHD STREAM-VAR STREAM=CHD SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VW1 STREAM-VAR STREAM=W1 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VW2 STREAM-VAR STREAM=W2 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VW3 STREAM-VAR STREAM=W3 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VW4 STREAM-VAR STREAM=W4 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VW7 STREAM-VAR STREAM=W7 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VW10 STREAM-VAR STREAM=W10 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE VHCL1 STREAM-VAR STREAM=HCL1 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE MCL2 MASS-FLOW STREAM=REAC1 SUBSTREAM=MIXED  &
    COMPONENT=CL2
  DEFINE MCH4 MASS-FLOW STREAM=REAC1 SUBSTREAM=MIXED  &
    COMPONENT=CH4
  DEFINE MH2O1 STREAM-VAR STREAM=H2O-1 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE MH2O2 STREAM-VAR STREAM=H2O-2 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
```

```
    VARIABLE=MASS-FLOW
DEFINE QHB2 BLOCK-VAR BLOCK=B2 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE QCB5 BLOCK-VAR BLOCK=B5 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE POWB8 BLOCK-VAR BLOCK=B8 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
DEFINE QCB9 BLOCK-VAR BLOCK=B9 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE POWB11 BLOCK-VAR BLOCK=B11 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
DEFINE QCB12 BLOCK-VAR BLOCK=B12 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
DEFINE QHB12 BLOCK-VAR BLOCK=B12 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
DEFINE QCB14 BLOCK-VAR BLOCK=B14 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
DEFINE QHB14 BLOCK-VAR BLOCK=B14 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
DEFINE QCB16 BLOCK-VAR BLOCK=B16 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
DEFINE QHB16 BLOCK-VAR BLOCK=B16 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
DEFINE CSTB18 CBLOCK-VAR CBLOCK= E-4 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
DEFINE FR11 BLOCK-VAR BLOCK=B4 SENTENCE=FRAC &
    VARIABLE=FRAC ID1=11
DEFINE QHB19 BLOCK-VAR BLOCK=B19 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE CSTB30 CBLOCK-VAR CBLOCK= E-10 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
DEFINE POWB30 BLOCK-VAR BLOCK=B30 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
DEFINE QCB31 BLOCK-VAR BLOCK=B31 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE QCB32 BLOCK-VAR BLOCK=B32 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE QCB35 BLOCK-VAR BLOCK=B35 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE CSTB35 CBLOCK-VAR CBLOCK= E-2 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
DEFINE FR3 BLOCK-VAR BLOCK=B3 SENTENCE=FRAC &
    VARIABLE=FRAC ID1=3
DEFINE QCB37 BLOCK-VAR BLOCK=B37 VARIABLE=QCALC &
    SENTENCE=PARAM
DEFINE CSTB40 CBLOCK-VAR CBLOCK= E-12 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
DEFINE POWB40 BLOCK-VAR BLOCK=B40 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
DEFINE CSTB51 CBLOCK-VAR CBLOCK= E-21 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
```

```
  DEFINE QCB51 BLOCK-VAR BLOCK=B51 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB51 BLOCK-VAR BLOCK=B51 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
  DEFINE CSTB55 CBLOCK-VAR CBLOCK= E-22 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE QCB55 BLOCK-VAR BLOCK=B55 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB55 BLOCK-VAR BLOCK=B55 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
  DEFINE CSTB56 CBLOCK-VAR CBLOCK= E-23 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE QCB56 BLOCK-VAR BLOCK=B56 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB56 BLOCK-VAR BLOCK=B56 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
  DEFINE CSTB57 CBLOCK-VAR CBLOCK= E-24 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE QCB57 BLOCK-VAR BLOCK=B57 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB57 BLOCK-VAR BLOCK=B57 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
; --------------------------------
;      INITIALIZING
; --------------------------------
F     IF (QHB2 .GT. 1E20) QHB2=0
F     IF (QCB5 .GT. 1E20) QCB5=0
F     IF (QCB9 .GT. 1E20) QCB9=0
F     IF (QHB19 .GT. 1E20) QHB19=0
F     IF (QCB31 .GT. 1E20) QCB31=0
F     IF (QCB37 .GT. 1E20) QCB37=0
; --------------------------------
;     VARIABLE DEFINITION
; --------------------------------
F     HR=8.15
F     CWASTE=0.23
F     CCL2=0.113
F     CCH4=0.0722
F     CCH3OH=0.235
F     CH2O=1.98E-4
F     CQH=5.96E-6
F     CQC=-6.59E-6
F     CPOW=0.052
F     RQ=1.76
F     RW=-2.88E-4
F     MHCL=MHCL+1
F     M55=M55+1
; --------------------------------
;      OPERATING COSTS
; --------------------------------
F     RAWD=MCL2*CCL2+MCH4*CCH4
```

```
F    RAWI=(MH2O1+MH2O2)*CH2O
F    RAW=RAWD+RAWI
F    WASTE=(VW1+VW2+VW3+VW4+VW7+VW10+VHCL1+VCH2+VCH2D+
   $  VCHCL3+VCHD)*CWASTE
F    B2=QHB2*CQH
F    B5=QCB5*CQC
F    B8=POWB8*CPOW
F    B9=QCB9*CQC*RQ+QCB9*RW*CPOW
F    B11=POWB11*CPOW
F    B12=QCB12*CQC*RQ+QCB12*RW*CPOW+QHB12*CQH
F    B14=QCB14*CQC+QHB14*CQH
F    B16=QCB16*CQC+QHB16*CQH
F    B19=QHB19*CHC
F    B30=POWB30*CPOW
F    B31=QCB31*CQC*RQ+QCB31*RW*CPOW
F    B32=QCB32*CQC
F    B35=QCB35*CQC
F    B37=QCB37*CQC
F    B40=POWB40*CPOW
F    B51=QCB51*CQC*RQ+QCB51*RW*CPOW+QHB51*CQC
F    B55=QCB55*CQC*RQ+QCB55*RW*CPOW+QHB55*CQH
F    B56=QCB56*CQC+QHB56*CQH
F    B57=QCB57*CQC+QHB57*CQH
F    UTIL1=B2+B5+B8+B9+B11+B12+B14+B16+B19+B30+B31
F    UTIL2=B32+B35+B37+B40+B51+B55+B56+B57
F    UTIL=UTIL1+UTIL2
F    OPCOST=(RAW+WASTE+UTIL)*HR
; --------------------------------
;      CAPITAL COSTS
; --------------------------------
F    B18=CSTB18*(1-FR11)*FR96
F    B30=CSTB30*(1-FR11)
F    B35=CSTB35*(1-FR3)
F    B40=CSTB40*(1-FR11)*FR96
F    B51=CSTB51*FR96*(1-FR11)
F    B55=CSTB55*FR96*(1-FR11)
F    B56=CSTB56*FR96*(1-FR11)
F    B57=CSTB57*FR96*(1-FR11)
F    TCI=B18+B30+B35+B40+B51+B55+B56+B57
F    TCI=TCI/1000
; --------------------------------
;      OBJECTIVE FUNCTION
; --------------------------------
F    NY=7
F    RINT=0.15
F    TAX=0.34
F    PV=0
F    DOPC=114100-OPCOST
F    DO 10 J=1,NY
F     DIF=1/((1+RINT)**J)
F     DEF=(2*(NY-J+1))/(NY*(NY+1))
```

```
F     PV=DIF*(TCI*DEF*TAX+DOPC*(1-TAX))
F 10  CONTINUE
F     VALUE=PV-TCI
   MAXIMIZE "VALUE"
   CONSTRAINTS  C-1
   VARY BLOCK-VAR BLOCK=B3 SENTENCE=FRAC VARIABLE=FRAC ID1=3
   LIMITS "0" "1"
   VARY BLOCK-VAR BLOCK=B4 SENTENCE=FRAC VARIABLE=FRAC ID1=11
   LIMITS "0" "1"
   VARY BLOCK-VAR BLOCK=B8 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "80" "200"
   VARY BLOCK-VAR BLOCK=B13 VARIABLE=TEMP SENTENCE=PARAM
   LIMITS "662" "932"
   VARY BLOCK-VAR BLOCK=B32 VARIABLE=TEMP SENTENCE=PARAM
   LIMITS "662" "932"
   VARY BLOCK-VAR BLOCK=B32 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "14.7" "45"

COMP-GROUP G1 CH4 CL2 HCL CH3CL CH2CL2 CHCL3

CONV-OPTIONS
   SQP MAXPASS=99990

CONVERGENCE OP SQP
   OPTIMIZE O-1
   TEAR 12 COMPS=G1 STATE=NONE

REACTIONS RSCH-1 POWERLAW
   REAC-DATA 1 PHASE=V CBASIS=MOLARITY
   REAC-DATA 2 PHASE=V CBASIS=MOLARITY
   REAC-DATA 3 PHASE=V CBASIS=MOLARITY
   REAC-DATA 4 PHASE=V CBASIS=MOLARITY
   RATE-CON 1 PRE-EXP=2.56E8 ACT-ENERGY=35260
   RATE-CON 2 PRE-EXP=6.28E7 ACT-ENERGY=30580
   RATE-CON 3 PRE-EXP=2.56E8 ACT-ENERGY=35260
   RATE-CON 4 PRE-EXP=2.93E8 ACT-ENERGY=37490
   STOIC 1 MIXED CH4 -1 / CL2 -1 / CH3CL 1 / HCL 1
   STOIC 2 MIXED CH3CL -1 / CL2 -1 / CH2CL2 1 / HCL 1
   STOIC 3 MIXED CH2CL2 -1 / CL2 -1 / CHCL3 1 / HCL 1
   STOIC 4 MIXED CHCL3 -1 / CL2 -1 / CCL4 1 / HCL 1
   POWLAW-EXP 1 MIXED CH4 1 / MIXED CL2 1
   POWLAW-EXP 2 MIXED CH3CL 1 / MIXED CL2 1
   POWLAW-EXP 3 MIXED CH2CL2 1 / MIXED CL2 1
   POWLAW-EXP 4 MIXED CHCL3 1 / MIXED CL2 1
```

# APPENDIX E
# INPUT FILE FOR SECTION II

```
TITLE 'Methyl Chloride Production - Section II'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=15000 MAX-ERRORS=1000000  &
  MAX-FORT-ERRORS=100000

DATABANKS AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  /  &
    INORGANIC

PROP-SOURCES AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  /  &
    INORGANIC

COMPONENTS
  H2O H2O H2O /
  HCL HCL HCL /
  CL2 CL2 CL2 /
  CH4 CH4 CH4 /
  CH3CL CH3CL CH3CL /
  CH2CL2 CH2CL2 CH2CL2 /
  CHCL3 CHCL3 CHCL3 /
  CCL4 CCL4 CCL4

FLOWSHEET
  BLOCK B1 IN=43 REAC1 OUT=1
  BLOCK B2 IN=1 OUT=2
  BLOCK B3 IN=2 OUT=3 5
  BLOCK B4 IN=7 OUT=11 25
  BLOCK B13 IN=5 OUT=6
  BLOCK B15 IN=34 OUT=CH3CL-C 94
  BLOCK B21 IN=30 45 OUT=40 31
  BLOCK B22 IN=94 OUT=CH2B 95
  BLOCK B23 IN=47 OUT=HCL2 34
  BLOCK B30 IN=41 OUT=26
  BLOCK B31 IN=26 OUT=100
  BLOCK B32 IN=3 OUT=7
  BLOCK B35 IN=6 OUT=9
  BLOCK B37 IN=25 OUT=41
  BLOCK B41 IN=40 OUT=43
  BLOCK B46 IN=95 OUT=CHB W9
  BLOCK B47 IN=100 OUT=96 89
  BLOCK B52 IN=CH3CLIN OUT=102
  BLOCK B53 IN=102 OUT=45
  BLOCK B54 IN=31 46 OUT=47
  BLOCK B58 IN=89 OUT=30 46

PROPERTIES NRTL-RK
```

```
STREAM REAC1
    SUBSTREAM MIXED TEMP=77 PRES=14.7
    MOLE-FLOW CL2 331 / CH4 450

STREAM CH3CLIN
    SUBSTREAM MIXED TEMP=77 PRES=14
    MOLE-FLOW CH3CL 1400

BLOCK B1 MIXER

BLOCK B54 MIXER

BLOCK B3 FSPLIT
    FRAC 3 1

BLOCK B4 FSPLIT
    FRAC 11 0

BLOCK B47 FSPLIT
    FRAC 96 0

BLOCK B2 HEATER
    PARAM TEMP=572 PRES=0

BLOCK B13 HEATER
    PARAM TEMP=842 PRES=0

BLOCK B31 HEATER
    PARAM TEMP=-58 PRES=0

BLOCK B37 HEATER
    PARAM TEMP=77 PRES=0

BLOCK B53 HEATER
    PARAM TEMP=-58 PRES=0

BLOCK B58 FLASH2
    PARAM PRES=0 DUTY=0

BLOCK B21 RADFRAC
    PARAM NSTAGE=10 ABSORBER=YES
    FEEDS 30 10 ON-STAGE / 45 1 ON-STAGE
    PRODUCTS 31 10 L / 40 1 V
    P-SPEC 1 14.7
    COL-SPECS Q1=0 QN=0 MOLE-RDV=1
    T-EST 10 -50

BLOCK B22 RADFRAC
    PARAM NSTAGE=40
    FEEDS 94 20 ON-STAGE
    PRODUCTS 95 40 L / CH2B 1 V
```

```
  P-SPEC 1 14.7
  COL-SPECS D:F=0.5 DP-STAGE=0.1 MOLE-RDV=1 MOLE-RR=1.3
  SPEC 1 MOLE-RECOV 0.99 COMPS=CH2CL2 STREAMS=CH2B
  VARY 1 D:F 0.001 0.999
  SIZE-DATA COND=YES REB=YES

BLOCK B15 DSTWU
  PARAM LIGHTKEY=CH3CL RECOVL=0.999 HEAVYKEY=CH2CL2  &
    RECOVH=0.001 PTOP=15 PBOT=15 NSTAGE=10

BLOCK B23 DSTWU
  PARAM LIGHTKEY=HCL RECOVL=0.9999 HEAVYKEY=CL2  &
    RECOVH=0.001 PTOP=15 PBOT=15 NSTAGE=10

BLOCK B46 DSTWU
  PARAM LIGHTKEY=CHCL3 RECOVL=0.999 HEAVYKEY=CCL4  &
    RECOVH=0.001 PTOP=15 PBOT=15 NSTAGE=10

BLOCK B32 RCSTR
  PARAM VOL=1600 TEMP=842 PRES=0
  REACTIONS RXN-IDS=RSCH-1

BLOCK B35 RPLUG
  PARAM TYPE=T-SPEC LENGTH=60 DIAM=3
  REACTIONS RXN-IDS=RSCH-1

BLOCK B30 COMPR
  PARAM TYPE=RIG-POLYTROP PRES=115 TEMP=275

BLOCK B41 COMPR
  PARAM TYPE=RIG-POLYTROP DELP=30

BLOCK B52 COMPR
  PARAM TYPE=RIG-POLYTROP PRES=14.7

PROJECT-DATE
  START MONTH=JANUARY YEAR=1995
  PURCHASE MONTH=JANUARY YEAR=1995

COST-INDEX
  EQUIPMENT

CBLOCK E-2 H-VESSEL
  SIZING-DATA VOL=1600
  REFERENCE BLOCK=B35

CBLOCK E-5 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B21
```

```
CBLOCK E-7 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B23

CBLOCK E-10 COMPR
  REFERENCE BLOCK=B30

CBLOCK E-13 COMPR
  REFERENCE BLOCK=B41

CBLOCK E-15 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B15

CBLOCK E-16 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B46

CBLOCK E-17 TRAY-TOWER
  SIZING-DATA
  REFERENCE BLOCK=B22

CBLOCK E-25 V-VESSEL
  SIZING-DATA VOL=500
  REFERENCE BLOCK=B58

FORTRAN INIT
  DEFINE QCB15 BLOCK-VAR BLOCK=B15 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB15 BLOCK-VAR BLOCK=B15 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
  DEFINE QCB22 BLOCK-VAR BLOCK=B22 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB22 BLOCK-VAR BLOCK=B22 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
  DEFINE QCB23 BLOCK-VAR BLOCK=B23 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB23 BLOCK-VAR BLOCK=B23 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
  DEFINE POWB30 BLOCK-VAR BLOCK=B30 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
  DEFINE QCB32 BLOCK-VAR BLOCK=B32 VARIABLE=QCALC &
    SENTENCE=PARAM
  DEFINE QCB35 BLOCK-VAR BLOCK=B35 VARIABLE=QCALC &
    SENTENCE=PARAM
  DEFINE POWB41 BLOCK-VAR BLOCK=B41 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
  DEFINE QCB46 BLOCK-VAR BLOCK=B46 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB46 BLOCK-VAR BLOCK=B46 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
```

```
    DEFINE POWB52 BLOCK-VAR BLOCK=B52 VARIABLE=IND-POWER  &
      SENTENCE=RESULTS
    DEFINE CSTB15 CBLOCK-VAR CBLOCK= E-15 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB21 CBLOCK-VAR CBLOCK= E-5 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB22 CBLOCK-VAR CBLOCK= E-17 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB23 CBLOCK-VAR CBLOCK= E-7 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB30 CBLOCK-VAR CBLOCK= E-10 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB35 CBLOCK-VAR CBLOCK= E-2 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB41 CBLOCK-VAR CBLOCK= E-13 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB46 CBLOCK-VAR CBLOCK= E-16 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
    DEFINE CSTB58 CBLOCK-VAR CBLOCK= E-25 VARIABLE=TOT-COST  &
      SENTENCE=RESULTS
F      QCB15=0
F      QHB15=0
F      QCB22=0
F      QHB22=0
F      QCB23=0
F      QHB23=0
F      POWB30=0
F      QCB32=0
F      QCB35=0
F      POWB41=0
F      QCB46=0
F      QHB46=0
F      POWB52=0
F      CSTB15=0
F      CSTB21=0
F      CSTB22=0
F      CSTB23=0
F      CSTB30=0
F      CSTB35=0
F      CSTB41=0
F      CSTB46=0
F      CSTB58=0
    EXECUTE FIRST

DESIGN-SPEC HCL
    DEFINE CH345 MOLE-FLOW STREAM=45 SUBSTREAM=MIXED  &
      COMPONENT=CH3CL
    DEFINE CH3IN MOLE-FLOW STREAM=CH3CLIN SUBSTREAM=MIXED  &
      COMPONENT=CH3CL
    DEFINE HCL30 MOLE-FLOW STREAM=30 SUBSTREAM=MIXED  &
      COMPONENT=HCL
```

```
F     CH3CL=HCL30*5.5
  SPEC "CH3IN" TO "CH3CL"
  TOL-SPEC "0.1"
  VARY MOLE-FLOW STREAM=CH3CLIN SUBSTREAM=MIXED
COMPONENT=CH3CL
  LIMITS "0" "10000"

CONSTRAINT C-1
  DEFINE MCH3C MOLE-FLOW STREAM=CH3CL-C SUBSTREAM=MIXED &
    COMPONENT=CH3CL
  DEFINE MCH3IN MOLE-FLOW STREAM=CH3CLIN SUBSTREAM=MIXED &
    COMPONENT=CH3CL
F     PROD=MCH3C-MCH3IN
  SPEC "PROD" EQ "160"
  TOL-SPEC "0.1"

OPTIMIZATION O-1
  DEFINE MCH3C MASS-FLOW STREAM=CH3CL-C SUBSTREAM=MIXED &
    COMPONENT=CH3CL
  DEFINE MCH3IN MASS-FLOW STREAM=CH3CLIN SUBSTREAM=MIXED &
    COMPONENT=CH3CL
  DEFINE VCH2B STREAM-VAR STREAM=CH2B SUBSTREAM=MIXED &
    VARIABLE=MASS-FLOW
  DEFINE VCHB STREAM-VAR STREAM=CHB SUBSTREAM=MIXED &
    VARIABLE=MASS-FLOW
  DEFINE VW9 STREAM-VAR STREAM=W9 SUBSTREAM=MIXED &
    VARIABLE=MASS-FLOW
  DEFINE VHCL2 STREAM-VAR STREAM=HCL2 SUBSTREAM=MIXED &
    VARIABLE=MASS-FLOW
  DEFINE MCL2 MASS-FLOW STREAM=REAC1 SUBSTREAM=MIXED &
    COMPONENT=CL2
  DEFINE MCH4 MASS-FLOW STREAM=REAC1 SUBSTREAM=MIXED &
    COMPONENT=CH4
  DEFINE QHB2 BLOCK-VAR BLOCK=B2 VARIABLE=QCALC &
    SENTENCE=PARAM
  DEFINE CSTB15 CBLOCK-VAR CBLOCK= E-15 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE QCB15 BLOCK-VAR BLOCK=B15 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB15 BLOCK-VAR BLOCK=B15 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
  DEFINE FR11 BLOCK-VAR BLOCK=B4 SENTENCE=FRAC  &
    VARIABLE=FRAC ID1=11
  DEFINE CSTB21 CBLOCK-VAR CBLOCK= E-5 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE CSTB22 CBLOCK-VAR CBLOCK= E-17 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE QCB22 BLOCK-VAR BLOCK=B22 VARIABLE=COND-DUTY &
    SENTENCE=RESULTS
  DEFINE QHB22 BLOCK-VAR BLOCK=B22 VARIABLE=REB-DUTY &
    SENTENCE=RESULTS
```

```
 DEFINE CSTB23 CBLOCK-VAR CBLOCK= E-7 VARIABLE=TOT-COST &
   SENTENCE=RESULTS
 DEFINE QCB23 BLOCK-VAR BLOCK=B23 VARIABLE=COND-DUTY &
   SENTENCE=RESULTS
 DEFINE QHB23 BLOCK-VAR BLOCK=B23 VARIABLE=REB-DUTY &
   SENTENCE=RESULTS
 DEFINE CSTB30 CBLOCK-VAR CBLOCK= E-10 VARIABLE=TOT-COST &
   SENTENCE=RESULTS
 DEFINE POWB30 BLOCK-VAR BLOCK=B30 VARIABLE=IND-POWER &
   SENTENCE=RESULTS
 DEFINE QCB31 BLOCK-VAR BLOCK=B31 VARIABLE=QCALC &
   SENTENCE=PARAM
 DEFINE QCB32 BLOCK-VAR BLOCK=B32 VARIABLE=QCALC &
   SENTENCE=PARAM
 DEFINE QCB35 BLOCK-VAR BLOCK=B35 VARIABLE=QCALC &
   SENTENCE=PARAM
 DEFINE CSTB35 CBLOCK-VAR CBLOCK= E-2 VARIABLE=TOT-COST &
   SENTENCE=RESULTS
 DEFINE FR3 BLOCK-VAR BLOCK=B3 SENTENCE=FRAC &
   VARIABLE=FRAC ID1=3
 DEFINE QCB37 BLOCK-VAR BLOCK=B37 VARIABLE=QCALC &
   SENTENCE=PARAM
 DEFINE CSTB41 CBLOCK-VAR CBLOCK= E-13 VARIABLE=TOT-COST &
   SENTENCE=RESULTS
 DEFINE POWB41 BLOCK-VAR BLOCK=B41 VARIABLE=IND-POWER &
   SENTENCE=RESULTS
 DEFINE FR96 BLOCK-VAR BLOCK=B47 SENTENCE=FRAC &
   VARIABLE=FRAC ID1=96
 DEFINE CSTB46 CBLOCK-VAR CBLOCK= E-16 VARIABLE=TOT-COST &
   SENTENCE=RESULTS
 DEFINE QCB46 BLOCK-VAR BLOCK=B46 VARIABLE=COND-DUTY &
   SENTENCE=RESULTS
 DEFINE QHB46 BLOCK-VAR BLOCK=B46 VARIABLE=REB-DUTY &
   SENTENCE=RESULTS
 DEFINE QCB53 BLOCK-VAR BLOCK=B53 VARIABLE=QCALC &
   SENTENCE=PARAM
 DEFINE CSTB58 CBLOCK-VAR CBLOCK= E-25 VARIABLE=TOT-COST &
   SENTENCE=RESULTS
; --------------------------------
;      INITIALIZING
; --------------------------------
F    IF (QHB2 .GT. 1E20) QHB2=0
F    IF (QCB31 .GT. 1E20) QCB31=0
F    IF (QCB37 .GT. 1E20) QCB37=0
F    IF (QCB53 .GT. 1E20) QCB53=0
F    IF (M55 .EQ. 0) M55=1
F    IF (MHCL .EQ. 0) MHCL=1
; --------------------------------
;    VARIABLE DEFINITION
; --------------------------------
F    HR=8.15
```

```
F    CWASTE=0.23
F    CCL2=0.113
F    CCH4=0.0722
F    CCH3OH=0.235
F    CH2O=1.98E-4
F    CQH=5.96E-6
F    CQC=-6.59E-6
F    CPOW=0.052
F    CPOW=0.052
F    RQ=1.76
F    RW=-2.88E-4
F    MHCL=MHCL+1
; --------------------------------
;      OPERATING COSTS
; --------------------------------
F    RAWD=MCL2*CCL2+MCH4*CCH4
F    RAWI=(MH2O1+MH2O2)*CH2O
F    RAW=RAWD+RAWI
F    WASTE=(VW9+VHCL2+VCH2B+VCHB)*CWASTE
F    B2=QHB2*CQH
F    B15=QCB15*CQC*RQ+QCB15*RW*CPOW+QHB15*CQH
F    B22=QCB22*CQC+QHB22*CQH
F    B23=QCB23*CQC*RQ+QCB23*RW*CPOW+QHB23*CQH
F    B30=POWB30*CPOW
F    B31=QCB31*CQC*RQ+QCB31*RW*CPOW
F    B32=QCB32*CQC
F    B35=QCB35*CQC
F    B37=QCB37*CQC
F    B41=POWB41*CPOW
F    B46=QCB46*CQC+QHB46*CQH
F    B53=QCB53*CQC*RQ+QCB53*RW*CPOW
F    UTIL=B2+B15+B22+B23+B30+B31+B32+B35+B37+B41+B46+B53
F    OPCOST=(RAW+WASTE+UTIL)*HR
; --------------------------------
;      CAPITAL COSTS
; --------------------------------
F    B15=CSTB15
F    B21=CSTB21*(1-FR96)*(1-FR11)
F    B22=CSTB22*(1-FR96)*(1-FR11)
F    B23=CSTB23*(1-FR11)
F    B30=CSTB30*(1-FR11)
F    B35=CSTB35*(1-FR3)
F    B41=CSTB41*(1-FR11)*(1-FR96)
F    B46=CSTB46*(1-FR11)*(1-FR96)
F    B58=CSTB58*(1-FR96)
F    TCI=B15+B21+B22+B23+B30+B35+B41+B46+B58
F    TCI=TCI/1000
; --------------------------------
;      OBJECTIVE FUNCTION
; --------------------------------
F    NY=7
```

```
F     RINT=0.15
F     TAX=0.34
F     PV=0
F     DOPC=114100-OPCOST
F     DO 10 J=1,NY
F       DIF=1/((1+RINT)**J)
F       DEF=(2*(NY-J+1))/(NY*(NY+1))
F       PV=DIF*(TCI*DEF*TAX+DOPC*(1-TAX))
F  10  CONTINUE
F     VALUE=PV-TCI
   MAXIMIZE "VALUE"
   CONSTRAINTS  C-1
   VARY BLOCK-VAR BLOCK=B3 SENTENCE=FRAC VARIABLE=FRAC ID1=3
   LIMITS "0" "1"
   VARY BLOCK-VAR BLOCK=B13 VARIABLE=TEMP SENTENCE=PARAM
   LIMITS "662" "932"
   VARY BLOCK-VAR BLOCK=B32 VARIABLE=TEMP SENTENCE=PARAM
   LIMITS "662" "932"
   VARY BLOCK-VAR BLOCK=B32 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "14.7" "45"
   VARY BLOCK-VAR BLOCK=B35 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "14.7" "45"
   VARY MOLE-FLOW STREAM=REAC1 SUBSTREAM=MIXED  &
        COMPONENT = CH4
   LIMITS "440" "475"
   VARY BLOCK-VAR BLOCK=B30 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "80" "200"

COMP-GROUP G2 HCL CH3CL CH2CL2 CHCL3

CONV-OPTIONS
   SQP MAXPASS=99990

CONVERGENCE D1 SECANT
   SPEC HCL

CONVERGENCE OP SQP
   OPTIMIZE O-1
   TEAR 30 COMPS=G2 STATE=NONE
   PARAM MAXPASS=99999

CONV-ORDER D1 OP

REACTIONS RSCH-1 POWERLAW
   REAC-DATA 1 PHASE=V CBASIS=MOLARITY
   REAC-DATA 2 PHASE=V CBASIS=MOLARITY
   REAC-DATA 3 PHASE=V CBASIS=MOLARITY
   REAC-DATA 4 PHASE=V CBASIS=MOLARITY
   RATE-CON 1 PRE-EXP=2.56E8 ACT-ENERGY=35260
   RATE-CON 2 PRE-EXP=6.28E7 ACT-ENERGY=30580
   RATE-CON 3 PRE-EXP=2.56E8 ACT-ENERGY=35260
```

```
RATE-CON 4 PRE-EXP=2.93E8 ACT-ENERGY=37490
STOIC 1 MIXED CH4 -1 / CL2 -1 / CH3CL 1 / HCL 1
STOIC 2 MIXED CH3CL -1 / CL2 -1 / CH2CL2 1 / HCL 1
STOIC 3 MIXED CH2CL2 -1 / CL2 -1 / CHCL3 1 / HCL 1
STOIC 4 MIXED CHCL3 -1 / CL2 -1 / CCL4 1 / HCL 1
POWLAW-EXP 1 MIXED CH4 1 / MIXED CL2 1
POWLAW-EXP 2 MIXED CH3CL 1 / MIXED CL2 1
POWLAW-EXP 3 MIXED CH2CL2 1 / MIXED CL2 1
POWLAW-EXP 4 MIXED CHCL3 1 / MIXED CL2 1
```

# APPENDIX F
# INPUT FILE FOR SECTION III

```
TITLE 'Methyl Chloride Production - Section III'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=15000 MAX-ERRORS=1000000  &
  MAX-FORT-ERRORS=100000

DATABANKS AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  / &
    INORGANIC

PROP-SOURCES AQUEOUS  / ASPENPCD  / PURECOMP  / SOLIDS  / &
    INORGANIC

COMPONENTS
  H2O H2O H2O /
  HCL HCL HCL /
  CL2 CL2 CL2 /
  CH4 CH4 CH4 /
  CH3CL CH3CL CH3CL /
  CH2CL2 CH2CL2 CH2CL2 /
  CHCL3 CHCL3 CHCL3 /
  CCL4 CCL4 CCL4 /
  CH3OH CH4O CH3OH

FLOWSHEET
  BLOCK B17 IN=REAC2 60 OUT=50
  BLOCK B25 IN=50 OUT=51
  BLOCK B26 IN=58 OUT=52
  BLOCK B27 IN=52 59 OUT=53
  BLOCK B28 IN=53 OUT=54 55
  BLOCK B29 IN=54 OUT=CH3CL-B W5
  BLOCK B33 IN=55 OUT=56 W6
  BLOCK B38 IN=57 OUT=59
  BLOCK B39 IN=51 OUT=57 58
  BLOCK B42 IN=56 OUT=60
  BLOCK B43 IN=61 OUT=REAC2 62
  BLOCK B44 IN=HCL-OH CL-CH OUT=44 61
  BLOCK B45 IN=44 OUT=REAC1 91

PROPERTIES NRTL-RK

STREAM CL-CH
  SUBSTREAM MIXED TEMP=77 PRES=14.7
  MOLE-FLOW CL2 331 / CH4 293

STREAM HCL-OH
  SUBSTREAM MIXED TEMP=77 PRES=14.7
  MOLE-FLOW HCL 194 / CH3OH 180
```

```
BLOCK B17 MIXER

BLOCK B39 FSPLIT
  FRAC 57 0

BLOCK B44 FSPLIT
  FRAC 44 0

BLOCK B29 SEP
  FRAC STREAM=CH3CL-B SUBSTREAM=MIXED COMPS=H2O HCL  &
    CL2 CH4 CH3CL CH2CL2 CHCL3 CCL4 CH3OH FRACS=0 0  &
    0 0 0.999 0 0 0 0

BLOCK B33 SEP
  FRAC STREAM=56 SUBSTREAM=MIXED COMPS=H2O HCL CL2  &
    CH4 CH3CL CH2CL2 CHCL3 CCL4 CH3OH FRACS=0 0.95  &
    0 0 0 0 0 0 0

BLOCK B43 SEP
  FRAC STREAM=REAC2 SUBSTREAM=MIXED COMPS=H2O HCL   &
    CL2 CH4 CH3CL CH2CL2 CHCL3 CCL4 CH3OH FRACS=0 1 0  &
    0 0 0 0 0 1

BLOCK B45 SEP
  FRAC STREAM=REAC1 SUBSTREAM=MIXED COMPS=H2O HCL  &
    CL2 CH4 CH3CL CH2CL2 CHCL3 CCL4 CH3OH FRACS=0 0  &
    1 1 0 0 0 0 0

BLOCK B25 HEATER
  PARAM TEMP=662 PRES=0

BLOCK B27 HEATER
  PARAM TEMP=90 PRES=0

BLOCK B28 FLASH2
  PARAM PRES=0 DUTY=0

BLOCK B26 RPLUG
  PARAM TYPE=ADIABATIC LENGTH=12 DIAM=10
  REACTIONS RXN-IDS=RSCH-2

BLOCK B38 RPLUG
  PARAM TYPE=T-SPEC LENGTH=12 DIAM=10
  REACTIONS RXN-IDS=RSCH-2

BLOCK B42 COMPR
  PARAM TYPE=RIG-POLYTROP DELP=30

PROJECT-DATE
  START MONTH=JANUARY YEAR=1995
  PURCHASE MONTH=JANUARY YEAR=1995
```

```
COST-INDEX
  EQUIPMENT

CBLOCK E-8 H-VESSEL
  SIZING-DATA VOL=950
  REFERENCE BLOCK=B26

CBLOCK E-9 V-VESSEL
  SIZING-DATA VOL=150
  REFERENCE BLOCK=B28

CBLOCK E-11 H-VESSEL
  SIZING-DATA VOL=950
  REFERENCE BLOCK=B38

CBLOCK E-14 COMPR
  REFERENCE BLOCK=B42

FORTRAN INIT
  DEFINE QCB38 BLOCK-VAR BLOCK=B38 VARIABLE=QCALC &
    SENTENCE=PARAM
  DEFINE POWB42 BLOCK-VAR BLOCK=B42 VARIABLE=IND-POWER &
    SENTENCE=RESULTS
  DEFINE CSTB26 CBLOCK-VAR CBLOCK= E-8 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE CSTB28 CBLOCK-VAR CBLOCK= E-9 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE CSTB38 CBLOCK-VAR CBLOCK= E-11 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
  DEFINE CSTB42 CBLOCK-VAR CBLOCK= E-14 VARIABLE=TOT-COST &
    SENTENCE=RESULTS
F    QCB38=0
F    POWB42=0
F    CSTB26=0
F    CSTB28=0
F    CSTB38=0
F    CSTB42=0
  EXECUTE FIRST

CONSTRAINT C-1
  DEFINE MCH3B MOLE-FLOW STREAM=CH3CL-B SUBSTREAM=MIXED &
    COMPONENT=CH3CL
F   PROD=MCH3B
  SPEC "PROD" EQ "160"
  TOL-SPEC "0.1"

OPTIMIZATION O-1
  DEFINE MCH3B MASS-FLOW STREAM=CH3CL-B SUBSTREAM=MIXED &
    COMPONENT=CH3CL
  DEFINE VW5 STREAM-VAR STREAM=W5 SUBSTREAM=MIXED &
```

```
       VARIABLE=MASS-FLOW
    DEFINE VW6 STREAM-VAR STREAM=W6 SUBSTREAM=MIXED  &
       VARIABLE=MASS-FLOW
    DEFINE MCH3OH MASS-FLOW STREAM=REAC2 SUBSTREAM=MIXED  &
       COMPONENT=CH3OH
    DEFINE MHCL MASS-FLOW STREAM=REAC2 SUBSTREAM=MIXED  &
       COMPONENT=HCL
    DEFINE QHB25 BLOCK-VAR BLOCK=B25 VARIABLE=QCALC  &
       SENTENCE=PARAM
    DEFINE CSTB26 CBLOCK-VAR CBLOCK= E-8 VARIABLE=TOT-COST  &
       SENTENCE=RESULTS
    DEFINE QCB27 BLOCK-VAR BLOCK=B27 VARIABLE=QCALC  &
       SENTENCE=PARAM
    DEFINE CSTB28 CBLOCK-VAR CBLOCK= E-9 VARIABLE=TOT-COST  &
       SENTENCE=RESULTS
    DEFINE FR44 BLOCK-VAR BLOCK=B44 SENTENCE=FRAC  &
       VARIABLE=FRAC ID1=44
    DEFINE M55 STREAM-VAR STREAM=55 SUBSTREAM=MIXED  &
       VARIABLE=MASS-FLOW
    DEFINE CSTB38 CBLOCK-VAR CBLOCK= E-11 VARIABLE=TOT-COST  &
       SENTENCE=RESULTS
    DEFINE FR57 BLOCK-VAR BLOCK=B39 SENTENCE=FRAC  &
      VARIABLE=FRAC  ID1=57
    DEFINE QCB38 BLOCK-VAR BLOCK=B38 VARIABLE=QCALC  &
       SENTENCE=PARAM
    DEFINE CSTB42 CBLOCK-VAR CBLOCK= E-14 VARIABLE=TOT-COST  &
       SENTENCE=RESULTS
    DEFINE POWB42 BLOCK-VAR BLOCK=B42 VARIABLE=IND-POWER  &
       SENTENCE=RESULTS
; ---------------------------------
;       INITIALIZING
; ---------------------------------
F     IF (QHB25 .GT. 1E20) QHB25=0
F     IF (QCB27 .GT. 1E20) QCB27=0
F     IF (M55 .EQ. 0) M55=1
F     IF (MHCL .EQ. 0) MHCL=1
; ---------------------------------
;     VARIABLE DEFINITION
; ---------------------------------
F     HR=8.15
F     CWASTE=0.23
F     CCL2=0.113
F     CCH4=0.0722
F     CCH3OH=0.235
F     CH2O=1.98E-4
F     CQH=5.96E-6
F     CQC=-6.59E-6
F     CPOW=0.052
F     CPOW=0.052
F     RQ=1.76
F     RW=-2.88E-4
```

```
F    MHCL=MHCL+1
F     COSHCL=(5.645E-6*(MHCL**0.7)+0.929*(MHCL**0.5)+4.437E-6*MHCL)
F   $  /MHCL
; ---------------------------------
;        OPERATING COSTS
; ---------------------------------
F    RAWD=MCH3OH*CCH3OH+COSHCL
F    RAWI=0
F    RAW=RAWD+RAWI
F    WASTE=(VW5+VW6)*CWASTE
F    B25=QHB25*CQH
F    B27=QCB27*CQC
F     B33=(5.645E-6*(M55**0.7)+0.929*(M55**0.5)+4.437E-6*M55)/M55
F    B38=QCB38*CQC
F    B42=POWB42*CPOW
F     UTIL=B25+B27+B33+B38+B42
F    OPCOST=(RAW+WASTE+UTIL)*HR
; ---------------------------------
;        CAPITAL COSTS
; ---------------------------------
F    B26=CSTB26*(1-FR57)
F    B28=(CSTB28+2E6)*(1-FR44)
F   B33=32633*((M55+MHCL)**0.6)
F    B38=CSTB38*(1-FR44)*FR57
F    B42=CSTB42*(1-FR44)
F    TCI=B26+B28+B33+B38+B42
F    TCI=TCI/1000
; ---------------------------------
;        OBJECTIVE FUNCTION
; ---------------------------------
F    NY=7
F    RINT=0.15
F    TAX=0.34
F    PV=0
F    DOPC=114100-OPCOST
F    DO 10 J=1,NY
F      DIF=1/((1+RINT)**J)
F      DEF=(2*(NY-J+1))/(NY*(NY+1))
F      PV=DIF*(TCI*DEF*TAX+DOPC*(1-TAX))
F  10  CONTINUE
F    VALUE=PV-TCI
  MAXIMIZE "VALUE"
  CONSTRAINTS  C-1
  VARY BLOCK-VAR BLOCK=B25 VARIABLE=TEMP SENTENCE=PARAM
  LIMITS "500" "700"
  VARY BLOCK-VAR BLOCK=B28 VARIABLE=PRES SENTENCE=PARAM
  LIMITS "14.7" "75"
  VARY BLOCK-VAR BLOCK=B27 VARIABLE=TEMP SENTENCE=PARAM
  LIMITS "30" "150"
```

```
 VARY MOLE-FLOW STREAM=HCL-OH SUBSTREAM=MIXED   &
      COMPONENT=HCL
 LIMITS "190" "205"
 VARY BLOCK-VAR BLOCK=B39 SENTENCE=FRAC VARIABLE=FRAC ID1=57
 LIMITS "0" "1"

COMP-GROUP G1 CH4 CL2
COMP-GROUP G2 HCL CH3CL CH2CL2 CHCL3
COMP-GROUP G3 HCL CH3CL CH3OH H2O

CONVERGENCE OP SQP
 OPTIMIZE O-1
 TEAR 53 COMPS=G3 STATE=NONE
 PARAM MAXPASS=99999 / MAXIT=60

REACTIONS RSCH-2 POWERLAW
 REAC-DATA 1 PHASE=V CBASIS=MOLARITY
 RATE-CON 1 PRE-EXP=2.52E10 ACT-ENERGY=38700
 STOIC 1 MIXED CH3OH -1 / HCL -1 / CH3CL 1 / H2O 1
 POWLAW-EXP 1 MIXED CH3OH 1 / MIXED HCL 1
```

# APPENDIX G

# INPUT FILE FOR HEAT INTEGRATION

```
TITLE 'HEAT INTEGRATION'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=15000.0 MAX-ERRORS=1000 MAX-FORT-ERR=1000

DATABANKS PURECOMP / AQUEOUS / SOLIDS / INORGANIC / &
    NOASPENPCD

PROP-SOURCES PURECOMP / AQUEOUS / SOLIDS / INORGANIC

COMPONENTS
  HCL HCL HCL /
  H2O H2O H2O /
  CH3CL CH3CL CH3CL /
  CH3OH CH4O CH3OH

FLOWSHEET
  BLOCK B1 IN=C1 OUT=1 2
  BLOCK B2 IN=1 3 OUT=4
  BLOCK B3 IN=H1 OUT=5 6
  BLOCK B4 IN=5 7 OUT=8
  BLOCK H1-C1 IN=6 B OUT=7
  BLOCK C1-H1 IN=2 A OUT=3
  BLOCK H1-CU IN=8 D OUT=H1OUT
  BLOCK C1-HU IN=4 C OUT=C1OUT

PROPERTIES NRTL-RK

STREAM C1
; This stream corresponds to stream 50 in superstructure
  SUBSTREAM MIXED TEMP=51.13 PRES=14.7
  MOLE-FLOW HCL 190.3896 / CH3OH 180.0

STREAM H1
; This stream corresponds to stream 52 in superstructure
  SUBSTREAM MIXED TEMP=1250.189 PRES=14.7
  MOLE-FLOW H2O 177.8697 / HCL 10.244 / CH3CL 177.8697

DEF-STREAMS HEAT A B C D

STREAM A
  INFO HEAT DUTY=6E7

STREAM B
  INFO HEAT DUTY=6E7

STREAM C
  INFO HEAT DUTY=.0
```

```
 STREAM D
   INFO HEAT DUTY=.0

 BLOCK B2 MIXER

 BLOCK B4 MIXER

 BLOCK B1 FSPLIT
   FRAC 2 1.0

 BLOCK B3 FSPLIT
   FRAC 6 1.0

 BLOCK C1-H1 HEATER
   PARAM PRES=.0

 BLOCK C1-HU HEATER
   PARAM PRES=.0

 BLOCK H1-C1 HEATER
   PARAM PRES=.0

 BLOCK H1-CU HEATER
   PARAM PRES=.0

 CONSTRAINT C1
   DEFINE C1OUT STREAM-VAR STREAM=C1OUT SUBSTREAM=MIXED  &
     VARIABLE=TEMP
   SPEC "C1OUT" EQ "696"
   TOL-SPEC "1"

 CONSTRAINT C2
   DEFINE H1OUT STREAM-VAR STREAM=H1OUT SUBSTREAM=MIXED  &
     VARIABLE=TEMP
   SPEC "H1OUT" EQ "139"
   TOL-SPEC "1"

 CONSTRAINT C3
   DEFINE QC1H1 INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=A
   DEFINE QH1C1 INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=B
   SPEC "QC1H1+QH1C1" EQ "0"
   TOL-SPEC "50"

 CONSTRAINT C4
   DEFINE T6 STREAM-VAR STREAM=6 SUBSTREAM=MIXED  &
     VARIABLE=TEMP
   DEFINE T3 STREAM-VAR STREAM=3 SUBSTREAM=MIXED  &
     VARIABLE=TEMP
F     C6=T6-T3
   SPEC "C6" GE "18"
   TOL-SPEC "0.01"
```

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```
CONSTRAINT C5
  DEFINE T7 STREAM-VAR STREAM=7 SUBSTREAM=MIXED &
    VARIABLE=TEMP
  DEFINE T2 STREAM-VAR STREAM=2 SUBSTREAM=MIXED &
    VARIABLE=TEMP
F     C5=T7-T2
  SPEC "C5" GE "18"
  TOL-SPEC "0.01"

OPTIMIZATION O-1
  DEFINE QC1HU INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=C
  DEFINE QH1CU INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=D
  DEFINE QC1H1 INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=A
  DEFINE T6 STREAM-VAR STREAM=6 SUBSTREAM=MIXED &
    VARIABLE=TEMP
  DEFINE T3 STREAM-VAR STREAM=3 SUBSTREAM=MIXED &
    VARIABLE=TEMP
  DEFINE T2 STREAM-VAR STREAM=2 SUBSTREAM=MIXED &
    VARIABLE=TEMP
  DEFINE T7 STREAM-VAR STREAM=7 SUBSTREAM=MIXED &
    VARIABLE=TEMP
  DEFINE T4 STREAM-VAR STREAM=4 SUBSTREAM=MIXED &
    VARIABLE=TEMP
  DEFINE T8 STREAM-VAR STREAM=8 SUBSTREAM=MIXED &
    VARIABLE=TEMP
;---------------------------------
;    VARIABLE DEFINITION
;---------------------------------
F     CQH=3.24E-6
F     CQC=-6.59E-6
F     U=149.67
F     FC=1.0
F     MS=1004.4
F     X1=0.65
F     X2=0.3333
F     HR=8.15
;---------------------------------
;    OPERATING COSTS
;---------------------------------
F     OPCOST=(QC1HU*CQH+QH1CU*CQC)*HR
;---------------------------------
;    CAPITAL COSTS
;---------------------------------
F     EF=(MS*101.3*FC)/280.0
F     LMC1H1=(ABS(T6-T3)*ABS(T7-T2)*((ABS(T6-T3)+ABS(T7-T2))/2))**X2
F     CC1H1=EF*((QC1H1/(U*LMC1H1))**X1)
F     TCI=CC1H1/1000
; --------------------------------
;      OBJECTIVE FUNCTION
; --------------------------------
```

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```
F     NY=7
F     RINT=0.15
F     TAX=0.34
F     PV=0
F     DOPC=1586-OPCOST
F     DO 10 J=1,NY
F       DIF=1/((1+RINT)**J)
F       DEF=(2*(NY-J+1))/(NY*(NY+1))
F       PV=DIF*(TCI*DEF*TAX+DOPC*(1-TAX))
F  10  CONTINUE
F     VALUE=PV-TCI
    MAXIMIZE "VALUE"
    CONSTRAINTS C1 / C2 / C3 / C4 / C5
    VARY INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=A
    LIMITS "0" "1E8"
    VARY INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=B
    LIMITS "-1E8" "0"
    VARY INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=C
    LIMITS "0" "1E8"
    VARY INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=D
    LIMITS "-1E8" "0"
    VARY BLOCK-VAR BLOCK=B3 SENTENCE=FRAC VARIABLE=FRAC ID1=6
    LIMITS "0" "1"
    VARY BLOCK-VAR BLOCK=B1 SENTENCE=FRAC VARIABLE=FRAC ID1=2
    LIMITS "0" "1"

CONV-OPTIONS
    SQP MAXPASS=99990
```

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# VITA

Mauricio Marcos Dantus Litwak

Candidate for the Degree of

Master of Science

Thesis: WASTE MINIMIZATION AND PROCESS INTEGRATION APPLIED TO THE RETROFIT DESIGN OF CHEMICAL PROCESSES

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Mexico City, Mexico, on September 11, 1968, the son of David Dantus and Reyna Litwak.

Education: Graduated from Colegio Israelita de México, Mexico City, Mexico in May 1987; received a Bachelor of Science degree in Chemical Engineering from Universidad Iberoamericana, Mexico City, Mexico in April 1993. Completed the requirements for the Master of Science degree with a major in Chemical Engineering at Oklahoma State University in December 1995.

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